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Perfluoroalkyl- and perfluoroalkylether-substituted quinoxalines

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Abstract

A series of perfluoroalkyl- and perfluoroalkylether-substituted quinoxalines was synthesized to determine the effect of the attachment of the perfluorinated unit to the heterocyclic ring (directly or via a phenyl group) and the effect of the nature of the perfluoroalkylether chain on the thermal and oxidative stability. Both model compounds and polymeric materials were investigated. Quinoxalines wherein the heterocyclic rings were bridged by polyperfluoroalkylethers with either two or three CF₂ groups separating the ether oxygen from the heterocyclic ring were thermally stable below 316 °C. A polyquinoxaline system linked by a $p-C_6H_4(CF_2)_3O(CF_2)_4O(CF_2)_3-p-C_6H_4$ chain exhibited thermal and thermal oxidative stability above 330 °C. Having two CF₂ groups separating the aromatic ring from the ether oxygen led to a significantly lower stability and difficulties in the intermediate tetraketone synthesis.

Keywords: Perfluoroalkyl-substituted quinoxalines; Perfluoroalkylether-substituted quinoxalines; IR spectroscopy; Mass spectrometry; Synthesis; Thermal stability; Oxidative stability

1. Introduction

The ultimate goal of this investigation was the development of perfluoropolyalkylether-linked quinoxalines for high-temperature elastomer applications. In such a system the aromatic rings provide means for chain extension and crosslinking sites while the perfluoroalkylether chains impart the low $T_{\rm g}$ characteristics required for the low-temperature elastomer performance. The wide liquid ranges and low pour points of perfluoropolyalkylethers are fully documented [1-5] and the thermal oxidative stabilities of quinoxalines are well established [6]. Although perfluoropolyalkylethers undergo decomposition in the presence of metals/metal alloys at elevated temperatures in oxidizing atmospheres, this problem can be completely eliminated by the use of additives [7]. Based on these premises the feasibility study of the concept was undertaken. Two types of polymeric arrangements were considered: type A wherein the attachments of perfluoropolyalkylether chains are via phenyl groups and type B wherein the perfluoropolyalkylether chains are directly linked to the heterocyclic rings.

In view of the diminished aromatic cluster, type B would be expected to possess lower T_g characteristics than the cor-



responding A structure. On the other hand, the direct attachment of the perfluorinated moieties to the heterocyclic ring provides potential hydrolytic susceptibility. The syntheses and evaluations of model compounds and polymeric systems corresponding to the above delineated arrangements and the effect of the nature of the bridging groups on the stabilities of the resultant quinoxalines are reported.

2. Results and discussion

Depicted below is the general reaction sequence leading to arrangement A.

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Depending on the nature of the materials desired, mono- or di-functional perfluorinated intermediates and either 1,2-phenylenediamine or 3,3'-diaminobenzidine were used. The simplest representative of a perfluoroalkyl-substituted quinoxaline is compound **I**.



The synthesis of the benzil, $n-C_8F_{17}C_6H_4C(O)C(O)C_6H_5$, was described earlier [8]. The next step proceeded readily employing 1,2-phenylenediamine. The overall yields and properties are summarized in Table 1. Compound I was stable at 371 °C over 72 h, as is evident from the compilation presented in Table 2. For the majority of the model compounds TGA data are included in Table 1; however, in view of the materials' volatility these are not illustrative of the thermal stability. On the other hand, the lower weight loss onset in air as compared to the inert atmosphere indicates oxidative instability. In the case of an involatile composition, the TGA data provide meaningful stability information.

To determine the effect of a perfluoroalkylether substituent on the quinoxaline stability, compound **II** was prepared; its thermal stability was comparable to that of the perfluoroalkyl analogue.



The optimum conditions for the formation of the intermediate, $n-C_8F_{17}OCF_2CF_2C_6H_4C(O)C(O)C_6H_5$ were described previously [8]. Based on the stability data of II, the perfluoropolyalkylether-bridged dumbbell quinoxaline III was synthesized next.



The intermediate $C_6H_5C(O)C(O)C_6H_4(CF_2CF_2O)_5CF_2-CF_2C_6H_4C(O)C(O)C_6H_5$, has been reported [8]. The yield of the tetraketone was increased to 24% by extending the reaction time to 160 h and by using a 6:1 mole ratio of 4-iodobenzil to the diiodide, $I(CF_2CF_2O)_5CF_2CF_2I$. Still, the overall yield of quinoxaline **III** was low at 13%. No attempts were made to optimize the process further since quinoxaline **III** exhibited low thermal stability as evidenced by the high volatiles production at 371 °C and 92% starting material recovery following exposure at 316 °C (Table 2).

In view of the above results, and in particular the low yield in the iodide coupling step, the process leading to arrangement B was investigated. The general synthesis path is presented below:



In a manner analogous to the studies carried out in the case of arrangement A and depending on the product required, mono- and di-functional perfluorinated intermediates and either 1,2-phenylenediamine or 3,3'-diaminobenzidine were employed. In all instances, regardless of the type of the perfluorinated starting material, the ethyl esters gave much higher yields of chloro intermediates than the corresponding methyl analogues in the 1,2-diketone production first reported by Chen and Tamborski [9].

The simplest quinoxaline, **IV**, obtained by reaction of the diketone, $n-C_7F_{15}C(O)C(O)C_6H_5$, with 1,2-phenylenediamine exhibited a reasonable thermal stability at 371 °C, with 91% starting material recovery.



At 343 °C, the extent of degradation was minimal. The material however was oxidatively unstable at 343 °C. The limited quantity of available oxygen in the test performed at 343 °C in air was responsible for the 59% starting material recovery.

Table 1	
Quinoxaline dat	a summary

ID	Compound		MW		Yield	M.p. (°C)	TGA	
	Type °	R	Calc.	Osm.	(%) -		Onset (°C) N ₂ /air	<i>T</i> _{1/2} (°C) ^b N ₂ /air
1	RA	$C_8F_{17}\phi$	700	695	57	161-162	-	
11	RA	$C_8F_{17}OC_2F_4\phi$	816	-	29	101	-	_
ш	ARA	$\phi(C_2F_4O)_5C_2F_4\phi$	1243	1300	13	91-193	270/265	410/403
IV	RA	$C_{7}F_{15}$	574	590	42	118-119	115/120	200/215
v	RAAR	C ₇ F ₁₅	1146	NA	65	> 200	265/115	366/362
VI	ARA	$(C_2F_4O)_3C_2F_4$	1091	1100	25	72–75	170/175	335/333
VII	(ARA) ₃	$(C_2F_4O)_5C_2F_4$	3828	4200	20	87-89	320/260	536/529
VIII	RA	$F[CF(CF_3)CF_2O]_2CF(CF_3)$	656	680	55	liquid	85/78	178/185
IX	ARA	$C_{1}F_{6}O(C_{4}F_{8}O)_{2}C_{1}F_{6}$	1158	1150	22	68-70	229/227	355/344
х	ARA	$\phi C_3 F_6 O(C_4 F_8 O)_2 C_3 F_6 \phi$	1311	1250	23	135-138	315/300	427/423
XI-1	$(ARA)_{37}$	$\phi C_1 F_6 O(C_4 F_8 O)_2 C_1 F_6 \phi$	1309 ^d	5400	18	> 200	395/390	612/601
XI-2	(ARA) _{10.0}	$\phi C_3 F_6 O(C_4 F_8 O)_2 C_3 F_6 \phi$	1309 ^d	13700	19	> 200	400/397	615/597
XI-3	(ARA) ₈₇	$\phi C_3 F_6 O(C_4 F_8 O)_2 C_3 F_6 \phi$	1309 ^d	12000	19	> 200	365/365	630 °/606
XI-4	$(ARA)_{117}$	$\phi C_3 F_6 O(C_4 F_8 O)_2 C_3 F_6 \phi$	1309 ^d	15300	20	> 200	375/-	625 °/-
XI-5	$(ARA)_{12,1}$	$\phi C_{3}F_{6}O(C_{4}F_{8}O)_{2}C_{3}F_{6}\phi$	1309 ^d	15900	20	> 200	365/-	625 °/-

^a Overall yield based on perfluoroalkyliodides for compounds I and II; all others on perfluoroalkyl or perfluoroalkylether methyl or ethyl esters. ^b $T_{1/2}$ is the temperature at which the weight loss equals one-half of the original weight under thermogravimetric analysis.





^d This is the molecular weight of the repeating unit.

^e This temperature corresponds to 40% weight loss.

Had sufficient oxygen been present, no quinoxaline would have survived.

Interaction of the diketone, $n-C_7F_{15}C(O)C(O)C_6H_5$, with 3,3'-diaminobenzidine gave V.



Its thermal stability was found to be strongly dependent on purity. Using a sample which was not rigorously purified resulted in extensive degradation at 343 °C, yet when a repeatedly recrystallized material was employed the extent of decomposition was minimal.

In the case of model compounds which were sufficiently volatile, the purity was determined by quantitative GC. To establish the inherent stability of a given arrangement, samples having purities >99% were tested. In those instances where the purity could not be accurately assessed, melting point, molecular weight, spectral analyses, elemental



analyses and the extent of purification were used as purity criteria.

The dumbbell, perfluoropolyalkylether-linked quinoxaline VI was obtained in 25% overall yield versus the 13% yield attained for the corresponding arrangement A, quinoxaline III.



Compound VI was unstable at 371 °C; its stability at 343 °C was poor, based on 47% starting material recovery. Even at 316 °C the compound exhibited a certain degree of instability (84% starting material recovery).

Although the model compound VI did not exhibit the required thermal stability, it was of importance to assess (a) the feasibility of producing a polyquinoxaline system and (b) the effect of molecular weight increase on the overall thermal stability. The reaction between the tetraketone,

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Stability testing results ^a

Table 2



 $C_6H_5C(O)C(O)CF_2CF_2(OCF_2CF_2)_5C(O)C(O)C_6H_5$, and 3,3'-diaminobenzidine was monitored by ultraviolet spectroscopy to elucidate the operative mechanism. Apparently, when the tetraketone is first introduced to the tetraamine, it quickly reacts with two molecules of 3,3'-diaminobenzidine to form the intermediate shown, where x = 1. At the stage when the ratio of the tetraketone to the tetraamine reaches 1:2, the 3,3'-diaminobenzidine is consumed, leaving all the available amino end-groups in the form of the above intermediate. As tetraketone addition continues, the x = 1 material combines with the additional tetraketone to form the x=3product which can subsequently generate the homologue wherein x = 7. In the test performed, the quantity of tetraketone employed was sufficient to form 0.554 mmol of material where x = 3 and 0.027 mmol of material where x = 7. A mixture of such composition, after end-capping with benzil, would have an average molecular weight of 4030 which is consistent with the measured molecular weight of 4200. This mechanism thus requires the compound having x=1 to be formed first, followed by the stepwise production of compositions with x = 3, x = 7, etc.

The polymerization was expected to give a broad spectrum of products, but the narrow melting range (87-89 °C) supports the formation of an essentially unimolecular species. This is further confirmed, as mentioned above, by the measured average molecular weight of 4200. These data are in agreement with the material being composed of 95.4% of the compound with x=3 (molecular weight 3828) and 4.6% with x=7 (molecular weight 8183).

The degree of degradation at 316 °C of VII was high as measured by the quantity of the volatiles produced. Comparing the quantity of volatiles in terms of the ratio of mmol per mmol of starting material used showed that VII is substantially less stable than VI (10.85 mmol versus 1.05 mmol; see Table 1). This comparison is not entirely valid since VII is of a substantially higher molecular weight than VI. If one considers that 'polymer' VII possesses three times as many sites to attack (CF_2 next to the ring) compared to VI and that each attack will result in three times as many volatiles (assuming complete degradation), the ratio of volatiles per mole of VII to that of VI should be 9:1. The actual ratio of volatiles was 10:1 which should account for the small proportion of the x = 7 component. These data indicate that the inherent stability of VII is essentially identical to that of VI. However, these results also illustrate that a low degree of degradation in a model compound can be translated into an extensive degradation in a polymer. This effect increases with molecular weight. TGA data are in good agreement with the sealed ampoule results. The onset of weight loss in an inert atmosphere at 325 °C fully supports the degree of decomposition reached during 72 h at 316 °C. As mentioned earlier, in the case of these relatively high molecular weight, involatile materials, TGA provides a valuable stability assessment.

The presence of a $-CF_2CF_2OCF_2CF_2O$ group adjacent to the heterocyclic ring was believed to be responsible for the observed low thermal stability. Earlier studies have shown [10–12] that heterocyclic ring attachment via a $-CF(CF_3)O$ entit provides increased thermal stability as compared to a $(CF_2)_n$ linkage. Unexpectedly, quinoxaline **VIII** exhibited poor thermal stability at 316° as evidenced by only 34% starting material recovery.



Apparently, in the case of the quinoxaline, the shielding by the trifluoromethyl substituent is insufficient to compensate for the single carbon atom separation between the heterocyclic ring and the ether oxygen.

The effect of three-carbon separation was investigated next using compound IX. This material exhibited thermal stability at 316 $^{\circ}$ C comparable to that of quinoxaline VI.



Table 3	
Polyquinoxaline XI series experimental data *	

Quinoxaline	Amine ^b	Ketone ^c	Ketone/	Temp.	Time (h)	Diamine ^d	Yield	MW
	(minor)		ratio	(0)	()	(minor)	(%)	
XI-1	0.75	0.857	1.15:1	45-50	48	0.65	90	5400
XI-2	0.798 1	0.837 0	1.05:1	50-55	91	0.46	94	13700
XI-3	0.852 2	0.869 3	1.02:1	50-55	165	0.37	94	12000
XI-4	0.828 8	0.829 2	1.00:1	50-55	168	_	97	15300
XI-5 °	0.834 5	0.834 5	1.00:1	100	168	-	89	15900

^a In a typical reaction, the tetraamine in hexafluoroisopropanol (8 ml) was added at room temperature to the tetraketone in hexafluoroisopropanol (7 ml) and glacial acetic acid (0.5 g) over 45 min. The mixture was stirred under reflux at the denoted temperature for the denoted time. To the cooled solution was added diamine followed by heating for 24–66 h. The product was isolated by precipitation into methanol (twice) and dried in vacuo at 95 °C. ^b 3,3'-Diaminobenzidine.

 $[C_6H_5C(0)C(0)C_6H_4C_3F_6OC_4F_8]_2O.$

^d 1,2-Phenylenediamine.

e This test was performed in a sealed ampoule.

Two different, highly purified samples gave starting material recovery of 75%-80%. Based on the above studies, it became apparent that quinoxaline systems represented by arrangement B, having the perfluoropolyalkylether bridge directly linked to the heterocyclic ring, possess unacceptably low thermal stabilities.

A quinoxaline such as X, representing arrangement A, would be expected to embody a higher thermal stability than the quinoxaline **III** in view of the three-carbon separation between the phenyl ring and ether oxygen.



Furthermore, the iodide-coupling step should proceed more readily than in the case of the ICF_2CF_2O -moiety. Both of these premises were fully validated by the experimental results. Most significantly, compound **X** was stable at 330 °C, both in inert and oxidizing atmospheres.

The next question was the feasibility of polymer formation and whether the stability exhibited by the model compound was also inherent to the polymer. Only limited investigations were carried out on the polymerization process, namely the reaction of the tetraketone, $C_6H_5C(O)C(O)C_6H_4C_3F_6O$ $(C_4F_8O)_2C_3F_6C_6H_4C(O)C(O)C_6H_5$, with 3,3'-diaminobenzidine, varying the reagents' stoichiometries and temperature. It is evident from the data compiled in Table 3 that the molecular weights of the polyquinoxalines increased as the ratio of the reactants approached unity; raising the temperature from 55 °C to 100 °C did not seem to have an effect. To determine the inherent thermal and oxidative stability of this system required skewed stoichiometries to allow for endcapping. This was accomplished in the case of quinoxalines XI-1, XI-2 and XI-3 by end-capping the diketone-terminated chains with 1,2-phenylenediamine.

Based on the stability evaluations given in Table 2 the polyquinoxalines are exceptionally stable, as shown by the

negligible production of volatiles and the essentially quantitative recovery of starting material exemplified by quinoxaline XI-1. Unfortunately, in the case of XI-2 the starting material could not be quantified due to the very low solubility of the residue both in hexafluorobenzene and hexafluoroisopropanol following the exposure to 316 °C. The same occurred at 330 °C in vacuum and at 316 °C in air. Polyquinoxaline XI-2 was not very soluble in $(CF_3)_2$ CHOH and C_6F_6 prior to heat exposure. It should be emphasized that its molecular weight is more than twice that of XI-1.

The TGAs indicate stabilities, both in inert atmosphere and in air, of the order of 390 °C for the end-capped materials. Polyquinoxalines **XI-4** and **XI-5** were not end-capped and this most likely led to the somewhat decreased thermal stabilities as determined by the TGA weight loss. These materials were prepared to investigate further the effect of stoichiometries and to assess the influence of temperature on the degree of polymerization. Based on the results generated by the polyquinoxaline **XI** series, the concept of perfluoropolyalkylether-linked quinoxalines for thermally and oxidatively stable polymeric systems is fully validated.

3. Experimental details

3.1. General

Operations involving moisture or air-sensitive materials were carried out either in an inert-atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass or in vacuo.

All the melting points are uncorrected and were determined in evacuated, sealed capillaries, unless otherwise stated. Infrared spectra (IR) were recorded using a Perkin-Elmer Corp. model 1330 infrared spectrophotometer; ultraviolet (UV) spectra were obtained using a Beckman Corp. model 35 spectrophotometer. Molecular weights were determined in hexafluorobenzene using a Mechrolab model 302 vapor pressure osmometer. Gas chromatography (GC) was performed by employing either a 10 ft. $\times 1/8$ in stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb GAW or a 3 ft \times 1/8 in stainless steel column packed with 3% Dexsil 300 on 100/120 mesh Chromosorb WAW using a programming rate of 8 °C min⁻¹ from 35-300 °C. The mass spectrometric analyses were obtained with a 21-491B double focusing mass spectrometer attached to a Varian Aerograph model 2700 gas chromatograph equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system. Thermal gravimetric analyses (TGA) were carried out in inert atmospheres and in air, from room temperature to 700 °C at 10 °C min⁻¹ with a Du Pont 990/951 system. Differential scanning calorimetry (DSC) was carried out using a Du Pont 990 system. Vacuum line techniques were utilized where applicable. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

3.2. Pyrolyses

The tests were performed in 18–20 ml ampoules. The samples were weighed in and the ampoules were then evacuated using the vacuum line assembly. If the test was to be conducted in air, dry air, 600 mmHg, was introduced at this stage. Otherwise, once good vacuum (~ 0.001 mmHg) was attained, the ampoules were sealed. Following heating, the ampoules were cooled to -196 °C, opened to the vacuum system and the -196 °C noncondensables, if any, separated and analyzed by infrared spectroscopy.

Subsequently, the contents were warmed to room temperature and the volatiles collected in the calibrated portion of the vacuum line. If the quantities were larger than 0.2 mmol, the condensables were fractionated through -78 °C cooled trap into -196 °C cooled traps. The fractions were analyzed by quantitative infrared spectroscopy. The starting material remaining in the involatile portion was quantified either by quantitative GC, using an internal standard, by quantitative DSC (decrease in the endotherm associated with fusion) or by quantitative infrared spectroscopy using a matched cell technique. The procedure used depended on the nature of the starting material. The tests are summarized in Table 2.

3.3. Starting materials

The n-C₈F₁₇I was obtained from Du Pont De Nemours and Co.; MeO₂C(CF₂CF₂O)₅CF₂CF₂CO₂Me and MeO₂C-(CF₂)₃O(CF₂)₄O(CF₂)₄O(CF₂)₃CO₂Me, products of Exfluor Research Corp., were provided by the US Air Force. 3,3'-Diaminobenzidine and 1,2-phenylenediamine were obtained from Aldrich Chemical Co. 3,3'-Diaminobenzidine was recrystallized from *m*-cresol, m.p. 175–176 °C. 1,2-Phenylenediamine was recrystallized from methanol, m.p. 100– 101 °C. 4-Iodobenzil was prepared using the procedure reported previously [8].

3.4. Preparation of quinoxaline I

In a nitrogen atmosphere, to a stirred solution of 4-perfluoro-n-octylbenzil (6.00 g, 9.55 mmol) in m-cresol (15 ml) was added at room temperature 1,2-phenylenediamine (1.08 g, 10.0 mmol) in m-cresol (15 ml). After stirring for 19 h the product was isolated by filtration, washed with methanol and purified by dissolving in methylene chloride followed by precipitation into methanol to give 5.03 g (78.2%) yield, purity >99%) of I, m.p. 161-162 °C; MW: Calc., 700.40; Found 695. IR (Kel-F/Nujol mull, cm^{-1}): 3057 (w); 2300 (w); 1963 (vw); 1936 (w); 1692 (vw); 1628 (vw); 1607 (w); 1554 (w); 1534 (w); 1478 (m); 1460 (vw); 1445 (w); 1407 (m); 1350 (m); 1298 (s); 1254 (vs); 1230 (vs); 1200 (vs); 1147 (vs); 1110 (s); 1091 (s); 1058 (m); 1047 (m); 1027 (m); 1019 (m); 977 (m); 962 (m); 943 (m); 929 (w); 891 (w); 869 (w); 850 (m); 830 (vw); 819 (vw); 810 (m); 799 (vw); 771 (s); 760 (s); 735 (m); 721 (w); 699 (s); 655 (s); 635 (m); 620 (w); 600 (w). MS (70 eV) m/e (relative intensity, ion): 700 (base, M); $681 (20.6\%, M-F); 331 (33.4\%, M-C_7F_{15}); 281 (44.4\%, M-C_7F_{15}); 281 (44.4\%, M-F_{15}); 281 (44.4\%, M-F_{15$ $M - C_8 F_{17}$; 179 (31.0%, $C_6 H_5 CNC_6 H_4$); 178 (12.4%, $C_6H_4CNC_6H_4$; 152 (16.8%, $CF_2C_6H_4CN$).

3.5. Preparation of quinoxaline II

In a nitrogen atmosphere, to a stirred solution of benzil, n- $C_8F_{17}OCF_2CF_2C_6H_4C(O)C(O)C_6H_5$, (660 mg, 0.82 mmol) in m-cresol (4.0 ml) at 30 °C was added 1,2-phenylenediamine (114 mg, 1.06 mmol) in *m*-cresol (4.0 ml). After stirring at 30 °C for 19 h, the product 360 mg was precipitated with methanol (20 ml) at 0 °C and isolated by filtration. Sublimation gave 300 mg (45% yield, purity 99.5%) of II, m.p. 101-102 °C. IR (Kel-F/Nujol mull, cm⁻¹): 3055 (vw); 2915 (vw); 1484 (w); 1450 (vw); 1412 (w); 1352 (m); 1334 (w); 1295 (m); 1210 (s); 1181 (s); 1160 (s); 1135 (w); 1113 (m); 1100 (m); 1063 (w); 1027 (w); 1008 (m); 981 (m); 976 (m); 960 (w); 933 (w); 883 (m); 848 (m); 836 (vs); 817 (vs); 805 (vs); 776 (m); 763 (m); 750 (w); 736 (m); 707 (m); 667 (m); 653 (w). MS (70 eV) m/e (relative intensity, ion): 816 (base, M); 797 $(25.5\%, M-F); 381 (15.9\%, M-C_8F_{17}O); 331 (17.6\%)$ $M - C_8F_{17}OCF_2$; 281 (50.8%, $M - C_8F_{17}OCF_2CF_2$); 179 (59.2%, C₆H₅CNC₆H₄); 178 (29.6%, C₆H₄CNC₆H₄); 152 $(33.5\%, CF_2C_6H_4CN).$

3.6. Preparation of quinoxaline III

 $C_6H_5C(O)C(O)C_6H_4(CF_2CF_2O)_5CF_2C_6H_4C(O)C-(O)C_6H_5$ (0.80 g, 0.72 mmol) was stirred with 1,2-phenylenediamine (0.20 g, 1.84 mmol) in *m*-cresol (15 ml) for 24 h at room temperature. Following removal of *m*-cresol at reduced pressure at 50 °C, the residue was treated with methanol to give quinoxaline **III** (0.48 g, 52% yield), m.p. 91.5– 93 °C. Due to the material's involatility, its purity (GC) and MS could not be determined. Analysis: Calc. for $C_{52}H_{26}F_{24}N_4O_5: C, 50.25; H, 2.11; F, 36.69\%; MW, 1242.83.$ Found: C, 50.25; H, 1.88; F, 36.47%; MW, 1300. IR (Kel-F/Nujol mull, cm⁻¹): 3060 (w); 3035 (w); 2260 (w); 1947 (vw); 1610 (w); 1550 (vw); 1475 (w); 1443 (w); 1406 (w); 1393 (vw); 1347 (m); 1326 (m); 1285 (s); 1238 (vs); 1208 (vs); 1142 (vs); 1125 (vs); 1108 (s); 1093 (s); 1057 (w); 1020 (m); 974 (s); 950 (m); 922 (w); 890 (vw); 842 (m); 809 (m); 768 (m); 756 (s); 715 (m); 698 (m); 678 (m); 640 (m).

3.7. Preparation of $n-C_7F_{15}C(O)CCl_2C_6H_5$

Under a nitrogen atmosphere, to α, α, α -trichlorotoluene (2.51 g, 12.8 mmol) in tetrahydrofuran (25 ml) and diethylether (25 ml) at – 111 °C was added n-butyllithium (5.5 ml, 2.5 M) over a 1 h period; stirring at – 111 °C was continued for another 1.5 h. Subsequently, n-C₇F₁₅CO₂CH₃ (4.8 g, 11.2 mmol) was introduced over 20 min; the reaction mixture was kept at – 111 °C for an additional 4 h. Following quenching with cold, concentrated hydrochloric acid (5 ml) in ethanol (10 ml), the solution was poured on to 2 M hydrochloric acid (100 ml) and isolated with diethylether to give 4.7 g (74% yield) of n-C₇F₁₅C(O)CCl₂C₆H₅.MS (70 eV) *m/e* (relative intensity, ion) (only ³⁵Cl ions listed): 537 (7.5%, M-F); 521 (22.0%, M-Cl); 169 (15.3%, C₃F₇); 159 (base, C₆H₅CCl₂); 152 (44.9%, C₆H₅CClCO); 124 (49.5%, C₆H₅CCl); 89 (51.6%, C₇H₅).

3.8. Preparation of $n-C_7F_{15}C(O)C(O)C_6H_5$

A mixture of $n-C_7F_{15}C(O)CCl_2C_6H_5$ (4.5 g, 8.1 mmol) and silver nitrate (5.5 g, 32 mmol) in ethanol (100 ml) and water (100 ml) was heated under gentle reflux for 64 h. After cooling to room temperature, the solid was filtered, washed with diethylether and the residue (5.0 g), obtained following the removal of solvents from the filtrate, was distilled to give 4.0 g (79% yield) of $n-C_7F_{15}C(O)C(O)C_6H_5$, b.p. 69-70 $^{\circ}C/0.001 \text{ mmHg}$. IR (capillary film, cm⁻¹): 3350 (w); 3080 (w); 2934 (vw); 2870 (vw); 1970 (w); 1753 (m); 1682 (s); 1596 (m); 1580 (w); 1490 (vw); 1452 (m); 1413 (w); 1366 (m); 1350 (vw); 1320 (m); 1240 (vs); 1200 (vs); 1149 (vs); 1109 (m); 1063 (m); 1026 (w); 1000 (m); 933 (w); 883 (m); 850 (w); 805 (m); 745 (m); 736 (m); 721 (m); 700 (w); 683 (m); 659 (m). MS (70 eV) m/e (relative intensity, ion): 503 (4.1%, M+1); 483 (8.2%, M-F); 169 (14%, C_3F_7); 131 (31.0%, C_3F_5); 119 (19.2%, C_2F_5); 105 (base, C₆H₅CO).

3.9. Preparation of quinoxaline IV

In a nitrogen atmosphere, to a stirred mixture of n-C₇F₁₅C(O)C(O)C₆H₅ (1.52 g, 3.02 mmol) and *m*-cresol (5 ml) was added a solution of 1,2-phenylenediamine (0.41 g, 3.80 mmol) in *m*-cresol (10 ml) over 15 min at room temperature. After 30 min, a thick, solid layer was formed on top of the reaction mixture. Stirring at room temperature was

continued for 22 h. The mixture was poured on to methanol (20 ml), filtered and the solid rinsed with an additional ~ 50 ml of methanol to give quinoxaline IV (1.0 g, 59% yield), m.p. 118-119 °C. Analysis: Calc. for C₂₁H₉F₁₅N₂: C, 43.91; H, 1.58; F, 49.62%; MW, 574.32. Found: C, 44.06; H, 1.44; F, 49.03%; MW, 590. IR (Kel-F/Nujol mull, cm⁻¹): 3055 (w); 1960 (vw); 1650 (vw); 1650 (w); 1535 (w); 1480 (w); 1460 (w); 1445 (w); 1400 (w); 1364 (m); 1350 (w); 1330 (w); 1305 (w); 1240 (s); 1220 (s); 1140 (s); 1130 (s); 1102 (m); 1083 (w); 1035 (w); 1015 (w); 1006 (w); 972 (m); 917 (w); 881 (vw); 848 (w); 810 (w); 792 (vw); 770 (m); 740 (w); 721 (w); 699 (m); 670 (vw); 640 (m). MS (70 eV) m/e (relative intensity, ion): 574 (99.4%, M); $555 (20.0\%, M-F); 255 (26.2\%, M-C_6F_{13}); 236 (10.5\%,$ $M - C_6 F_{14}$; 205 (base, $M - C_7 F_{15}$); 179 (26.8%, $M - C_7 F_{15} CN$; 152 (14.8%, $C_6 H_4 NCCF_2$).

3.10. Preparation of quinoxaline V

In a nitrogen atmosphere, to 3,3'-diaminobenzidine (0.40 g, 1.87 mmol) in m-cresol (10 ml) was added n- $C_7F_{15}C(O)C(O)C_6H_5$ (2.11 g, 4.21 mmol) in *m*-cresol (5 ml). Heavy precipitation formed after one-half of the tetraketone solution was added. After stirring for 24 h at room temperature, the reaction mixture was poured on to methanol (50 ml). The precipitated product was filtered, washed with 50 ml of methanol and dried in vacuo to give V (1.93 g, 92%) yield). The material was insoluble in Freon-113, methylene chloride, benzene and hexafluorobenzene. It was recrystallized from hexafluoroisopropanol/ethanol, m.p. >200 °C. Due to the compound's involatility, the purity (GC) and MS could not be determined. Analysis: Calc. for C42H16F30N4: C, 43.99; H, 1.41; F, 49.71%. Found: C, 43.96; H, 1.27; F, 49.66%. IR (Kel-F/Nujol mull, cm^{-1}): 3055 (vw); 2260 (vw); 1610 (w); 1532 (w); 1477 (w); 1443 (vw); 1420 (w); 1395 (vw); 1365 (m); 1350 (m); 1320 (m); 1243 (s); 1215 (s); 1190 (s); 1140 (s); 1126 (vw); 1105 (s); 1080 (w); 1037 (w); 1010 (m); 970 (m); 895 (vw); 885 (w); 850 (w); 835 (m); 805 (w); 795 (w); 766 (m); 738 (m); 720 (m); 698 (m); 670 (w); 643 (w).

3.11. Preparation of C₆H₅CCl₂C(0)CF₂CF₂(0CF₂CF₂)₅C(0)CCl₂C₆H₅

Under a nitrogen atmosphere, to α, α, α -trichlorotoluene (11.15 g, 57.04 mmol) in tetrahydrofuran (125 ml) and diethylether (125 ml) at -111 °C was added n-butyllithium (25 ml, 2.5 M) over 1 h; stirring at -111 °C was continued for an additional 1 h. Subsequently, EtO₂C(CF₂CF₂O)₅-CF₂CC₂Et (29.34 g, 35.51 mmol) was added over 20 min and the reaction mixture was then stirred for 3 h at -111 °C. Following quenching with cold, concentrated hydrochloric acid (10 ml) in ethanol (20 ml), the mixture was poured into 2 M hydrochloric acid (250 ml) and the product isolated with diethylether to give 35.65 g (95% yield). Distillation resulted in 21.3 g (57% yield) (b.p. 159–162 °C/0.001

mmHg) of $C_6H_5CCl_2C(0)CF_2CF_2(OCF_2CF_2)_5C(0)$ -CCl₂C₆H₅. MS (70 eV) *m/e* (relative intensity, ion) (only ³⁵Cl ions listed): 1035 (1.4%, M – F); 1019 (7.8%, M – Cl); 519 (9.3%, C₆H₅CCl₂COCF₂CF₂(OCF₂CF₂)₂); 403 (14.7%, C₆H₅CCl₂COCF₂CF₂OCF₂CF₂); 287 (15.4%, C₆H₅CCl₂COCF₂CF₂); 159 (base, C₆H₅CCl₂); 124 (45.2%, C₆H₅CCl); 89 (57.5%, C₇H₅).

3.12. Preparation of $C_6H_5C(O)C(O)CF_2CF_2(OCF_2CF_2)_5C(O)C(O)C_6H_5$

A mixture of $C_6H_5CCl_2C(0)CF_2CF_2(0CF_2CF_2)_5$ -C(O)CCl₂C₆H₅ (9.2 g, 8.7 mmol) was stirred with silver nitrate (11.8 g, 69.6 mmol) in ethanol (150 ml) and water (150 ml) under gentle reflux for 94 h. After cooling to room temperature and filtration followed by washing with diethylether (150 ml), the organic layer was separated, washed with water, dried over anhydrous MgSO4 and the solvent removed in vacuo. Distillation of the residue gave $C_{6}H_{5}C(0)C(0)CF_{2}CF_{2}(0CF_{2}CF_{2})_{5}C(0)C(0)C_{6}H_{5}(5.2)$ g, 68% yield), b.p. 130-133 °C/0.001 mmHg. IR (capillary film, cm⁻¹): 3480 (vw); 3350 (vw); 3070 (w); 2920 (vw); 2850 (vw); 1967 (w); 1752 (m); 1684 (s); 1596 (m); 1580 (m); 1453 (m); 1320 (s); 1205 (vs); 1145 (vs); 1027 (w); 1006 (w); 998 (vw); 983 (w); 933 (w); 856 (m); 780 (w); 754 (w); 714 (m); 684 (m); 665 (m). MS (70 eV) m/e (relative intensity, ion): 927 (5.8%, M-F); 465 (14.4%, $C_6H_5COCOCF_2CF_2$ (OCF₂CF₂)₂); 349 (15.9%, C_6H_5 -COCOCF₂CF₂OCF₂CF₂); 233 (17.1%, C₆H₅COCOCF₂- CF_2 ; 105 (base, C_6H_5CO).

3.13. Preparation of quinoxaline VI

Under a nitrogen atmosphere, to a solution of C₆H₅- $C(O)C(O)CF_2CF_2(OCF_2CF_2)_5C(O)C(O)C_6H_5$ (2.21 g, 2.34 mmol) in m-cresol (5 ml) was added 1,2-phenylenediamine (602 mg, 5.57 mmol). After stirring at room temperature for 24 h, the mixture was poured on to stirred methanol (25 ml). No precipitate formed; the solvents were removed at 50 °C in vacuo. Treatment of the residue with methanol (10 ml) gave a white solid (1.12 g), m.p. 72-75 °C, purity 99.4% (GC). Analysis: Calc. for C₄₀H₁₈F₂₄N₄O₅: C, 44.05; H, 1.67; F, 41.81%; MW, 1090.62. Found: C, 44.12; H, 1.60; F, 40.91%; MW, 1100. IR (Kel- $F/Nujol mull, cm^{-1}$: 3060 (w); 1547 (m); 1480 (m); 1460 (vw); 1443 (m); 1356 (m); 1317 (s); 1220 (vs); 1140 (vs); 1098 (s); 1075 (w); 1035 (w); 1015 (m); 1005 (m); 954 (s); 937 (s); 887 (w); 844 (w); 800 (vw); 770 (m); 720 (w); 700 (m); 683 (m); 662 (w). MS (70 eV) m/e(relative intensity, ion): 1052 (8.0%, M-2F); 885 (3.5%, $M - C_6H_4N_2C_2C_6H_5$; 545 (28.5%, $C_6H_4N_2C_2(CF_2CF_2O)_3$ - CF_3 ; 421 (18.1%, $C_6H_4N_2C_2C_6H_5CF_2CF_2OCF_2CF_2$); 305 (28.5%, C₆H₄N₂C₂C₆H₅CF₂CF₂); 255 (19.7%, C₆H₄N₂- $C_2C_6H_5CF_2$; 205 (base, $C_6H_4N_2C_2C_6H_5$); 179 (33.0%, $C_6H_4NCC_6H_5$).

3.14. Preparation of quinoxaline VII

Under a nitrogen atmosphere, the tetraketone, C₆H₅- $C(O)C(O)CF_2CF_2(OCF_2CF_2)_5C(O)C(O)C_6H_5$, (0.87 g, 0.92 mmol) in hexafluoroisopropanol (5 ml) was added dropwise to a solution of 3,3'-diaminobenzidine (0.26 g, 1.21 mmol) in hexafluoroisopropanol (5 ml) over a period of 15 min. Both reagents prior to mixing and following the addition were subjected to UV analysis. Based on the absence of the 312 nm absorption, characteristic of 3,3'-diaminobenzidine, after addition, it is evident that the latter was completely consumed. The appearance of an absorption at 269 nm confirmed the formation of quinoxaline. The absorbance of 0.558 (1/5000 dilution with ethanol) corresponded to a concentration of 4×10^{-2} M ($\epsilon = 6.70 \times 10^4$) of quinoxaline with respect to the standard. After stirring for 18 h at room temperature, the reaction mixture was again sampled (diluted 1/ 8000 in hexafluoroisopropanol). The absorbance at 268 nm was 0.310. After stirring for an additional 5 h, the absorption was essentially unchanged (absorbance 0.325, 1/8000 dilution with hexafluoroisopropanol). Since a 20% excess of 3,3'-diaminobenzidine was used, the polymer would be expected to be amine-terminated. To obtain nonfunctional end-groups, benzil (0.17 g, 0.81 mmol) in hexafluoroisopropanol (1 ml) was added. After additional 16 h, the reaction mixture was concentrated to one-half of its volume and dripped into vigorously stirred methanol (50 ml) to give 1.08 g of a pale yellow solid. The process was repeated by dissolving the solid in hexafluoroisopropanol (3.5 ml) and dripping into methanol (35 ml). This resulted in a pale yellow solid (0.67 g, 55% yield), m.p. 87-89 °C; MW, 4200. IR (Kel-F/Nujol mull, cm^{-1}): 3060 (w); 1770 (vw); 1610 (m); 1540 (m); 1475 (m); 1444 (m); 1419 (w); 1390 (w); 1345 (m); 1316 (m); 1205 (s); 1125 (s); 1008 (m); 935 (m); 890 (w); 832 (m); 804 (w); 766 (m); 720 (m); 698 (m).

3.15. Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2C_6H_5$

Using the conditions described for the preparation of $C_6H_5CCl_2C(0)CF_2CF_2(OCF_2CF_2)_5C(0)CCl_2C_6H_5$, the ester, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2Et$, (4.53 g, 8.65 mmol) was added to the product of the reaction of α, α, α -trichlorotoluene (2.21 g, 11.4 mmol) with n-butyllithium (5 ml, 2.5 M). The yield of $C_3F_7OCF(CF_3)CF_2OCF-(CF_3)C(0)CCl_2C_6H_5$ was 73% (4.21 g). MS (70 eV) m/e (relative intensity, ion) (only ³⁵Cl ions listed): 619 (6.2%, M-F); 603 (21.5%, M-Cl); 335 (7.7%, $C_3F_7OCF(CF_3)CF_2)$; 169 (56.3%, C_3F_7); 159 (base, $C_6H_5CCl_2$); 152 (53.4%, C_6H_5CClCO); 124 (48.1%, C_6H_5CCl).

3.16. Preparation of $C_3F_2OCF(CF_3)C(O)C(O)C_6H_5$

Using the conditions described for the preparation of $C_6H_5C(O)C(O)CF_2CF_2(OCF_2CF_2)_5C(O)C(O)C_6H_5$, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2C_6H_5$ (4.2 g, 6.6 mmol) was treated with silver nitrate (6.2 g, 36.5 mmol) in aqueous ethanol for 91 h. This resulted in a 78% yield (3.0 g) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C(O)C_6H_5$, b.p. 49–50 °C/0.001 mmHg. IR (capillary film, cm⁻¹): 3065 (vw); 1752 (m); 1685 (s); 1597 (m); 1580 (vw); 1452 (m); 1330 (s); 1300 (s); 1235 (vs); 1200 (vs); 1155 (vs); 1125 (s); 1090 (m); 1028 (w); 992 (s); 978 (s); 933 (vw); 850 (m); 810 (w); 787 (w); 744 (m); 730 (w); 705 (w); 683 (m); 660 (m). MS (70 eV) *m/e* (relative intensity, ion): 585 (1.7%, M+H); 565 (8.2%, M-F); 399 (5.7%, M-C_3F_7O); 233 (15.7%, CFCF_3COCOC_6H_5); 169 (34.0%, C_3F_7); 150 (23.9%, C_3F_6); 105 (base, C_6H_5CO).

3.17. Preparation of quinoxaline VIII

Under a nitrogen atmosphere, 1,2-phenylenediamine (0.46 g, 4.34 mmol) in m-cresol (10 ml) was added to a stirred solution of C₃F₇OCF(CF₃)CF₂OCF(CF₃)C(O)C(O)C₆H₅ (2.01 g, 3.44 mmol) in m-cresol (10 ml); stirring at room temperature was continued for 24 h. After removal of mcresol under reduced pressure, the viscous residue (2.2 g) was purified by silica gel column chromatography (2.5 $cm \times 29$ cm) using diethylether/hexanes (1:3) as eluent to give 2.0 g (91% yield, purity 99.9%) of VIII. Analysis: Calc. for C₂₂H₉F₁₇N₂O₂: C, 40.26; H, 1.38; F, 49.21%; MW, 656.33. Found: C, 40.38; H, 1.41; F, 50.56%; MW, 680. IR (capillary film, cm^{-1}): 3063 (m); 3030 (w); 1610 (w); 1540 (m); 1497 (vw); 1480 (m); 1460 (w); 1445 (m); 1400 (w); 1350 (s); 1330 (vs); 1300 (vs); 1220 (vs); 1150 (vs); 1120 (vs); 1068 (s); 1035 (m); 1015 (s); 991 (vs); 980 (vs); 950 (s); 917 (w); 886 (m); 810 (m); 800 (m); 763 (vs); 750 (s); 698 (s); 664 (w); 648 (w); 630 (w); 610 (w). MS (70 eV) m/e (relative intensity, ion): 656 $(83.6\%, M); 637 (9.9\%, M-F); 471 (10.2\%, M-C_3F_7O);$ $(29.8\%, M-C_3F_7OCFCF_3CF_2O); 205$ (base, 305 $C_6H_4N_2C_2C_6H_5$; 179 (27.8%, $C_6H_4NCC_6H_5$); 178 (19.8%, $C_6H_4NCC_6H_4$; 169 (26.6%, C_3F_7).

3.18. Preparation of $[C_6H_5CCl_2C(0)C_3F_6OC_4F_8]_2O$

Using the conditions described for the preparation of $C_6H_5CCl_2C(0)CF_2CF_2(OCF_2CF_2)_5C(0)CCl_2C_6H_5$, the ester, [MeO₂CC₃F₆OC₄F₈]₂O, (12.9 g, 14.9 mmol) was added to the product of the reaction of α, α, α -trichlorotoluene (6.70 g, 34.3 mmol) with n-butyllithium (15 ml, 2.5 M, 37.5 mmol). The yield of [C₆H₅CCl₂C(0)C₃F₆OC₄F₈]₂O was 65% (10.8 g). MS (70 eV) *m/e* (relative intensity, ion) (only ³⁵Cl ions listed): 1051 (23.4%, M-Cl-HCl); 337 (21.5%, C₆H₅CCl₂COC₃F₆); 301 (13.5%, C₆H₄CCl-

 COC_3F_6 ; 201 (29%, $C_6H_4CClCOCF_2$); 159 (base, $C_6H_5CCl_2$); 124 (28.6%, $C_6H_5CCl_2$).

3.19. Preparation of $[C_6H_5C(O)C(O)C_3F_6OC_4F_8]_2O$

Using the conditions described for the preparation of $C_6H_5C(0)C(0)CF_2CF_2(0CF_2CF_2)_5C(0)C(0)C_6H_5$ $[C_6H_5CCl_2C(0)C_3F_6OC_4F_8]_2O$ (10.8 g, 9.61 mmol) was treated with silver nitrate (13.2 g, 77.7 mmol) in aqueous ethanol for 41 h. This resulted in a 61% yield (5.9 g) of $[C_6H_5C(0)C(0)C_3F_6OC_4F_8]_2O$, b.p. 163–165 °C/0.001 mmHg. IR (capillary film, cm^{-1}): 3480 (w); 3070 (w); 1780 (vw); 1757 (m); 1687 (s); 1600 (m); 1585 (w); 1455 (m); 1345 (s); 1287 (s); 1215 (vs); 1150 (vs); 1124 (vs); 1055 (vw); 1040 (vw); 1025 (w); 1001 (w); 954 (m); 933 (vw); 888 (m); 855 (m); 812 (w); 717 (m); 684 (m); 666 (w). MS (70 eV) m/e (relative intensity, ion): 995 (5.3%, M-F; 881 (3.2%, C₃F₆OC₄F₈OC₄F₈OC₃F₆COCOC₆H₅); 715 (1.6%, $C_4F_8OC_4F_8OC_3F_6COCOC_6H_5$); 499 (7.1%, $C_6H_5COCOC_3F_6OC_4F_8$; 283 (24.2%, $C_6H_5COCOC_3F_6$); 255 (29.2%, C₆H₅COC₃F₆); 105 (base, C₆H₅CO).

3.20. Preparation of quinoxaline IX

Under a nitrogen atmosphere, to $[C_6H_5C(O)C(O)-C_3F_6OC_4F_8]_2O$ (1.84 g, 1.81 mmol) in *m*-cresol (15 ml) was added 1,2-phenylenediamine (0.48 g, 4.45 mmol) in *m*-cresol (10 ml); the reaction mixture was stirred at room temperature for 22 h. After removal of *m*-cresol at reduced pressure at 60–70 °C, to the cooled residue was added methanol (10 ml). The resultant solid was filtered and washed several time with methanol.

Crystallization from methanol followed by drying at 40 °C for 3 h gave 1.14 g (54% yield) of a white solid, m.p. 72–74 °C (purity >99%, GC). Analysis: Calc. for $C_{42}H_{18}F_{28}N_4O_3$: MW, 1158.64. Found: MW, 1150. IR (Kel-F/Nujol mull, cm⁻¹): 3060 (w); 1610 (vw); 1545 (w); 1482 (w); 1464 (w); 1447 (w); 1405 (w); 1344 (m); 1326 (w); 1297 (m); 1285 (m); 1266 (m); 1235 (s); 1205 (s); 1190 (s); 1168 (s); 1146 (s); 1111 (s); 1093 (w); 1078 (w); 1056 (vw); 1034 (vw); 1013 (vw); 1003 (w); 997 (w); 972 (vw); 957 (vw); 932 (m); 906 (m); 882 (vw); 865 (m); 810 (w); 791 (w); 770 (s); 714 (m); 700 (m); 678 (w). MS (70 eV) *m/e* (relative intensity, ion): 1158 (89.7%, M); 1139 (17.6%, M-F); 355 (24.2%, C₆H₄N₂C₂C₆H₅C₃F₆); 205 (base, C₆H₄N₂C₂C₆H₅); 179 (14.7%, C₆H₄NCC₆H₅).

3.21. Preparation of $[AgO_2CC_3F_6OC_4F_8]_2O$

To a stirred solution of the diacid, $[HO_2CC_3F_6OC_4F_8]_2O$, (14.3 g, 17.1 mmol) in water (125 ml; titrated to pH 9.05 with ~2.5 M NaOH) was added AgNO₃ (8.7 g, 51 mmol, in 9 ml of water) at 10 °C over ~10 min. Precipitation occurred immediately; stirring was continued for 1 h. The solid was isolated by filtration, washed with water and dried in vacuo (<0.001 mmHg) for 6 h to give 16.6 g (92% yield)

3.22. Preparation of $[IC_3F_6OC_4F_8]_2O$

A mixture of finely ground iodine (9.3 g, 36.5 mmol) together with the silver salt $[AgO_2CC_3F_6OC_4F_8]_2O(7.00 \text{ g},$ 6.65 mmol) was placed on top of iodine (8.0 g) in a 45 mm ampoule; additional iodine (1.3 g) was put on top of the mixture. The ampoule was then attached to a nitrogen bypass, placed in an oil bath (preheated to 120 °C) and heated for 2 h. This was followed by 3 h at 140 °C. After cooling, all the material was extracted with Freon-113 (30 ml). Solvent removal in vacuo resulted in 5.88 g (88% yield) of [IC₃F₆OC₄F₈]₂O (purity 94%, GC). Treatment with copper bronze, followed by filtration and washing with Freon-113, removal and distillation) solvent gave (after $[IC_{3}F_{6}OC_{4}F_{8}]_{2}O$, 5.05 g (76% yield); b.p. 60-62 °C/0.001 mmHg. IR (capillary film, cm⁻¹): 1327 (s); 1307 (s); 1286 (s); 1195 (vs); 1150 (vs); 1125 (s); 1095 (vw); 1060 (m); 1025 (m); 952 (m); 933 (vw); 910 (vw); 890 (m); 827 (m); 795 (m); 747 (m); 711 (m); 685 (vw); 668 (m). MS (70 eV) m/e (relative intensity, ion): 1002 (74.5%, M); 277 (base, C_3F_6I); 177 (40.1%, CF_2I); 150 (24.8%, C_3F_6); 127 (41.4%, I); 100 (45.7%, C₂F₄).

3.23. Preparation of $[C_6H_5C(O)C(O)C_6H_4C_3F_6OC_4F_8]_2O$

Under a nitrogen atmosphere, a mixture of 4-iodobenzil (7.46 g, 29.8 mmol), copper bronze (5.78 g, 91.0 mmol) and $[IC_3F_6OC_4F_8]_2O$ (13.55 g, 13.5 mmol) in anhydrous dimethylsulfoxide (13.5 ml) was stirred at 105-119 °C for 24 h. After heating, two layers were present. Analysis by gas chromatography showed a trace of product in the top layer; the bottom layer consisted of 90% product. Dichloromethane (70 ml) was added to the bottom layer, the solution filtered and the remaining dimethylsulfoxide removed by washing with water. After drying with MgSO4 and solvent-removal, followed by heating in vacuo (<0.001 mmHg) for 4 h at 110 °C, 11.74 g of residue (purity, 94%, GC) was obtained. Purification by silica gel column chromatography (110 g, 48 $cm \times 2.8 cm$) gave $[C_6H_5C(0)C(0)C_6H_4C_3F_6OC_4F_8]_2O$ (6.78 g, 43% yield), m.p. 63-65 °C (purity 99.5%, GC) eluted in 1:1 diethylether/hexane. IR (Kel-F/Nujol mull, cm⁻¹): 3340 (vw); 3065 (w); 1679 (s); 1615 (vw); 1600 (m); 1583 (w); 1510 (vw); 1453 (m); 1415 (m); 1350 (m); 1323 (w); 1297 (m); 1270 (w); 1208 (vs); 1183 (vs); 1150 (s); 1125 (s); 1073 (vw); 1046 (w); 1017 (vw); 1000 (vw); 967 (m); 956 (m); 934 (vw); 910 (vw); 900 (vw); 870 (m); 840 (m); 792 (m); 755 (m); 717 (s); 683 (w); 672 (w); 659 (w). MS (70 eV) m/e (relative intensity,

3.24. Preparation of quinoxaline X

In an inert atmosphere, to a stirred solution of $[C_{6}H_{5}C(O)C(O)C_{6}H_{4}C_{3}F_{6}OC_{4}F_{8}]_{2}O(3.12 \text{ g}, 2.67 \text{ mmol})$ and glacial acetic acid (1 ml) in m-cresol (30 ml) was added 1,2-phenylenediamine (0.58 g, 5.36 mmol) in m-cresol (30 ml) over a period of 30 min. After stirring for an additional 2 h at room temperature, the reaction mixture was stirred at 45-50 °C for 18 h under nitrogen bypass. Following removal of m-cresol under reduced pressure, the viscous residue was added dropwise to vigorously stirred methanol (100 ml). The filtered solid (2.8 g, 80% yield), m.p. 118-122 °C, was recrystallized from benzene/hexane to give 0.83 g (24%) yield) of X, m.p. 135-137 °C. Analysis: Calc. for C₅₄H₂₆F₂₈N₄O₃: C, 49.48; H, 2.00; F, 40.59%; MW, 1310.84. Found: C, 49.99; H, 1.88; F, 41.01%; MW, 1300. IR (Kel- $F/Nujol, cm^{-1}$: 3050 (vw); 1938 (vw); 1610 (vw); 1480 (w); 1447 (vw); 1409 (w); 1400 (vw); 1347 (m); 1290 (m); 1230 (s); 1200 (s); 1180 (s); 1142 (s); 1113 (s); 1055 (w); 1019 (w); 977 (m); 970 (m); 945 (vw); 927 (vw);910 (vw);890 (vw);880 (vw);836 (m);811 (vw); 770 (m); 759 (m); 740 (w); 699 (m); 677 (w).

3.25. Quinoxaline XI series

The experimental details are summarized in Table 3. The characterization and stability data are presented in Tables 1 and 2. Polyquinoxaline **XI-1**, representative of the series, IR (Kel-F/Nujol, cm⁻¹): 3053 (vw); 1610 (w); 1475 (w); 1446 (vw); 1410 (w); 1342 (s); 1286 (s); 1220 (vs); 1180 (vs); 1145 (vs); 1117 (vs); 1076 (w); 1055 (m); 1035 (w); 1026 (w); 1017 (m); 977 (m); 953 (m); 932 (m); 889 (s); 839 (m); 830 (w); 802 (m); 768 (m); 696 (m); 673 (w).

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