1,1'-DISUBSTITUTED 2,2'-DI(n-PERFLUOROPROPYL)-5,5'-BIBENZIMIDAZOLYLS

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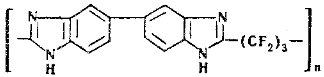
The synthesis of 4,4'-di(methylamino)- and 4,4'-dianilino-3,3'-diaminobiphenyls is described. The condensation of the tetraaminobiphenyls mentioned with phenyl perfluorobutyrate has given, respectively, 1,1'-dimethyl- and 1,1'-diphenyl-2,2'-(n-perfluoropropyl)-5,5'-bibenzimidazolyls. A study of the thermal stability of the 2-perfluoroalkylbenzimidazoles has shown that the replacement of the hydrogen of the imino group in these compounds by a methyl or a phenyl radical considerably increases their heat stability.

Unexpectedly, the poly[2,2'-(perfluorotrimethylene)-5,5'-bibenzimidazolyl] (I) synthesized in our laboratory by the condensation of diphenyl perfluoroglutarate with 3,3'-diaminobenzidine [1] proved to be thermally unstable and underwent far-reaching degradation accompanied by the evolution of hydrogen fluoride between 220 and 250° C. The same polymer was described by other authors [2, 3] almost simultaneously with our work.

It is probable that the thermal instability of the polymer I is due to condensation reactions taking place at high temperatures through the mobile hydrogen atoms of the imino groups of the benzimidazole rings and the fluorine atoms of the perfluorocarbon chains. To check this hypothesis, it was decided to compare the thermal stabilities of low-molecular-weight model fluorinated benzimidazoles containing an unsubstituted imino group with the thermal stabilities of their N-substituted derivatives in which the imino group was blocked by the introduction of a methyl or a phenyl radical so that the splitting out of hydrogen fluoride at the expense of the hydrogen atom of the imino group became impossible. In addition, the splitting out of hydrogen fluoride at the expense of the hydrogen atoms present in the substituent of the imino group should be highly obstructed.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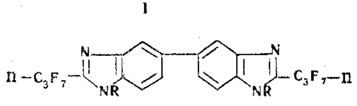
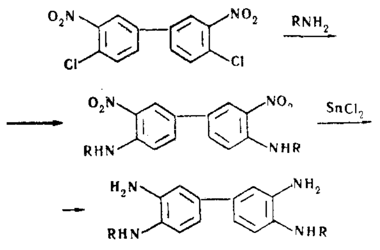

IIIa R = CH_3; b R = C_6H_5

With this aim, we synthesized 2-trifluoromethyl- and N-methyl-2-trifluoromethylbenzimidazoles, 1,3-di(2-benzimidazolyl)perfluoropropane [4], and N,N'-dimethyl-1,3-di(2-benzimidazolyl)perfluoropropane [4] and also 2-trifluoromethyl-benzoxazole [5].

In addition, by methylating 2,2'-di(perfluoropropyl)-5,5'-bibenzimidazolyl (or the corresponding 5,6' or 6,6' compounds) [4] (II) with diazomethane under the conditions described previously [4], we attempted to obtain its N,N'-dimethyl-substituted derivative. The methylation of compound II took place very smoothly but, as was to be expected [6], a mixture of isomers which was impossible to separate by crystallization was formed. Consequently, we synthesized the 1,1'-disubstituted 2,2'-di(perfluoropropyl)-5,5'-bibenzimidazolyls (IIIa, b) of interest to us from tetraaminobiphenyls partially substituted at the nitrogen atoms, 4,4'-di(methylamino)-3,3'-diaminobiphenyl (IVa) and 4,4'-dianilino-3,3'-diaminobiphenyl (IVb). The tetraamines IVa, b were obtained by the action of methylamine and aniline, respectively, on 4,4'-dichloro-3,3'-dinitrobiphenyl (this compound was synthesized from 3,3'-dinitrobenzidine [7] as described previously [8] with a yield of 50%) followed by reduction with stannous chloride in accordance with the following scheme:


IVa R = CH_3; b R = C_6H_5

By condensing compounds IVa, b with phenyl perfluorobutyrate [9] we synthesized, respectively, 1,1'-dimethyl-2,2'-di(perfluoropropyl)-5,5'-bibenzimidazolyl (IIIa) and 1,1'-diphenyl-2,2'-di(perfluoropropyl)-5,5'-bibenzimidazolyl (IIIb), modelling the fluorinated polybenzimidazole I substituted on the nitrogen atoms.

The determination of the thermal stability of the 2-perfluoroalkylbenzimidazoles was carried out in sealed Pyrex glass tubes evacuated to a pressure of 10^{-3} mm. The degradation temperature was taken as the temperature at which a measurable amount of gas (0.1–0.2 ml) was formed by a ~0.1 g sample in 1 hr. The degradation products of some compounds were analyzed by mass-spectrometric and gas-chromatographic methods.

As was found, 2-trifluoromethylbenzimidazole decomposes even at 280–300° C with the formation of HF. N-Methyl-2-trifluoromethylbenzimidazole is stable up to 450° C. Above this temperature, it undergoes degradation, evolving CH_4, CHF_3, and HF. The latter, on reaction with the glass, gives CO, CO_2, and SiF_4. 1,3-Di(2-benzimidazolyl)perfluoropropane is thermally stable up to 300° C and its N,N'-dimethyl-substituted derivative up to 390° C. 2,2'-Di(perfluoropropyl)-1,1'-diphenyl-5,5'-bibenzimidazolyl (IIIb) undergoes no changes up to 420° C. The thermal stability of 2-trifluoromethylbenzoxazole is similar to that of N-methyl-2-trifluoromethylbenzimidazole, degradation beginning at 440–450° C.

The results given show that the blocking of the imino group of 2-perfluoroalkylbenzimidazoles by the introduction of a methyl or phenyl radical does in fact greatly increase their thermal stability. Consequently, it might be expected that N-substituted fluorinated polybenzimidazoles will also prove more heat-stable than the fluorinated polybenzimidazole I. The synthesis and properties of such polymers is described elsewhere [10].

EXPERIMENTAL

4,4'-Di(methylamino)-3,3'-dinitrobiphenyl. With ice cooling, dry methylamine was passed into 48 ml of absolute ethanol until the increase in weight was 9 g (0.3 mole). This solution was stirred in a 100-ml stainless steel autoclave while 4.95 g (16 mM) of 4,4'-dichloro-3,3'-dinitrobiphenyl [8], mp 234°–235° C (from dimethylformamide) was added, and then the mixture was heated at 180° C (bath temperature) for 6 hr. Then it was filtered and the residue was boiled several times with a tenfold amount of water until the filtrate was pale yellow, after which it was dried. This gave a cherry-red microcrystalline powder sparingly soluble in organic solvents. Yield 82%, mp 276° C (decomp.). Found, %: C 55.28; H 4.70; N 18.18. Calculated for $C_{14}H_{14}N_4O_4$, %: C 55.63; H 4.66; N 18.52%.

4,4'-Di(methylamino)-3,3'-diaminobiphenyl (IVa). a) A three-necked flask with a thermometer and a stirrer was charged with 55 ml of concentrated HCl and 23.6 g of crystalline stannous chloride and, with stirring and cooling, 5 g (~17 mM) of 4,4'-di(methylamino)-3,3'-dinitrobiphenyl was added slowly to the resulting solution in such a way that the temperature of the reaction mixture did not exceed 40° C. Then it was stirred at 40° C for another hour and filtered, the brown filtrate was saturated with hydrogen chloride at 0° C and kept for 1 1/2 hr at 0° C, and the crystals of complex salt that had deposited were filtered off with suction and dissolved in 125 ml of water. The solution was boiled with carbon and was saturated with hydrogen chloride again as described above, and it was then left at 3°–5° C for 12–15 hr. The crystalline precipitate that had deposited was separated off and dissolved in 125 ml of water and, with water cooling, 30 g of 85% potassium hydroxide in 70 ml of water was added to give a strongly alkaline reaction. The amine, obtained in the form of a microcrystalline precipitate, was washed with water to neutrality, dried in vacuum in the dark, and recrystallized from anhydrous xylene (1 : 65). Yield 1.65 g (41%). The substance melted at 183°–185° C after gradually darkening. Found, %: C 69.36; H 7.48; N 23.14. Calculated for $C_{14}H_{18}N_4$, %: C 69.36; H 7.50; N 23.13.

Compound IV is sparingly soluble in the majority of organic solvents, with the exception of dimethylformamide, and almost insoluble in water. It darkens on storage in the air and in the light.

b) A 50-ml steel autoclave was charged with 0.5 g (~1.7 mM) of the dinitro compound, 0.15 g of Raney nickel catalyst and 10 ml of anhydrous dimethylformamide and was placed in an oscillating furnace. Reduction was carried out at ~95° C with an initial hydrogen pressure of 8 atm. After 3–4 hr, the reaction was complete. The resulting solution was filtered, the solvent was eliminated in vacuum in a current of argon, and the residue was recrystallized twice from xylene. The yield of IVa was 0.21 g (52%), mp 182°–184° C.

1,1'-Dimethyl-2,2'-di(n-perfluoropropyl)-5,5'-bibenzimidazolyl (IIIa). A mixture of 1.174 g (4.85 mM) of **IVa** and 2.813 g (9.7 mM) of phenyl perfluorobutyrate [9] was heated in a flask with an air condenser protected by a calcium chloride tube in a current of argon at a bath temperature of 185°–190° C for 2 hr, and the reaction product was dissolved in chloroform, washed several times with 5% sodium hydroxide solution and then with water to neutrality, and dried with magnesium sulfate. Then the chloroform was driven off in a current of argon, and the residue (2.37 g) was crystallized from ethanol (1 : 10) to give **IIIa**, yield 47%, mp 226°–227° C. After additional recrystallization from ethanol and then from ethyl acetate, the mp rose to 228°–229° C. Found, %: C 44.43; H 2.02; N 9.46; F 44.36. Calculated for $C_{22}H_{12}N_4F_{14}$, %: C 44.10; H 2.02; N 9.37; F 44.47. Compound IIIa is readily soluble in acetone and glacial acetic acid, moderately soluble in benzene, and sparingly soluble in heptane.

4,4'-Dianilino-3,3'-dinitrobiphenyl. A mixture of 9.39 g (30 mM) of 4,4'-dichloro-3,3'-dinitrobiphenyl and 49.5 ml (~0.5 mole) of freshly-distilled aniline was boiled in an atmosphere of nitrogen under reflux for 6 hr and was then left overnight. The dark brown pasty mass obtained was filtered with suction and the residue on the filter was washed with methanol until the filtrate was pale yellow. It was then boiled with 200 ml of distilled water. The solid matter was filtered off, washed with distilled water until the Beilstein test for halogen was negative, dried, and recrystallized several times from dioxane (1 : 10). The 4,4'-dianilino-3,3'-dinitrobiphenyl formed bright red platelike crystals. Yield 55%, mp 211°–212° C. Found, %: C 67.47; H 4.37; N 13.04. Calculated for $C_{24}H_{18}N_4O_4$, %: C 67.61; H 4.25; N 13.14. The substance is readily soluble in aniline, pyridine, and dioxane, sparingly soluble in benzene and ether, and practically insoluble in methanol and water.

4,4'-Dianilino-3,3'-diaminobiphenyl (IVb). A three-necked flask with a dropping funnel, reflux condenser, and stirrer was charged with 3.84 g (9 mM) of 4,4'-dianilino-3,3'-dinitrobiphenyl and 150 ml of of peroxide-free tetrahydrofuran. The mixture was heated until dissolution was complete and then, with stirring, 15 g of crystalline stannous chloride in 31.5 ml of concentrated HCl was added and the mixture was boiled with stirring for 2 1/2 hr. During the heating, the bright red color of the solution changed to yellowish, and a white precipitate deposited from it. The reaction mixture was cooled to ~20° C and the precipitate of complex salt was filtered off with suction, dried in vacuum, and boiled with 45 ml of 30% potassium hydroxide solution in a current of nitrogen for 1 1/2 hr. The amine, obtained in the form of an amorphous precipitate, was washed in water to neutrality, dissolved in tetrahydrofuran (1 : 10) that had been distilled in a current of nitrogen, and precipitated with 50 ml of ethanol. Yield 1.73 g (52%) The substance melted at 202°–203° C after gradually darkening. Found, %: C 78.42; H 6.02; N 15.59. Calculated for $C_{24}H_{22}N_4$, %: C 78.66; H 6.05; N 15.29. Compound IVb is readily soluble in tetrahydrofuran in the cold and in ethanol on heating and is almost insoluble in water. It is stable on storage in the dark.

1,1'-Diphenyl-2,2'-di(n-perfluoropropyl)-5,5'-bibenzimidazolyl (IIIb). A mixture of 1.77 g (4.85 mM) of IVb and 2.81 g (9.7 mM) of phenyl perfluorobutyrate was heated in a flask with an air condenser protected with a calcium chloride tube at 190°-200° C (bath temperature) for 3 hr. The reaction product was dissolved in chloroform and the solution was washed several times with 5% sodium hydroxide solution and then with water to neutrality and was dried with magnesium sulfate, after which the chloroform was driven off in vacuum and the residue was crystallized from ethanol. The yield of IIIb was 35%, mp 177°–178° C. Found, %: C 52.84; H 2.11; N 7.59; F 36.51. Calculated for $C_{32}H_{16}F_{14}N_4$, %: C 53.19; H 2.23; N 7.75; F 36.82. The substance is readily soluble in chloroform and ethyl acetate and insoluble in water.

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