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[A0037]

Synthesis of 1,2,4,5-benzenetetracarboxylic dianhydride – 4,4'-diaminodiphenyl ether 1 : 2 and 2 : 1 condensation products.

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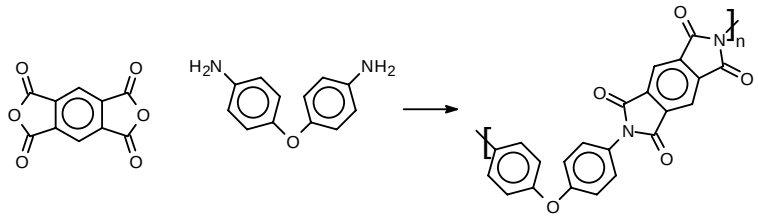
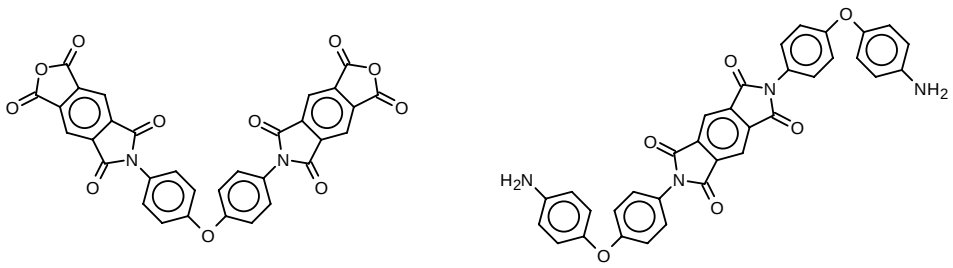
Abstract. Lowest oligomers of pyromellitic anhydride with oxydianiline, - 1 : 2 and 2 : 1 condensation products were synthesized.

Reaction of 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic anhydride, **I**) and 4,4'-diaminodiphenyl ether (oxydianiline, **II**) 1 : 1 mixture gives polylimide (**III**) well-known as Kapton. Polyimides are widely used for many purposes, for example, Kapton films used in cosmic space technology as important components for fabrication of materials for space satellites thermal insulation [1, 2].



I **II** **III**

The quality of polyimide **III** depends from content of low-molecular oligomers, beginning from lowest oligomers **IV** and **V**.



IV **V**

We have synthesized both above oligomers. Condensation of excess **I** with **II** gives oligomer with terminal anhydride groups (**IV**). When for condensation excess of **II** was employed, oligomer with terminal amino groups (**V**) was formed. Due to bad solubility of starting compounds, especially **I**, condensation proceeds in high-boiling solvents, which are inert to reaction components, such as halogenated aromatics. Nitroaromatics are not inert to amines at elevated temperatures and so, are less suitable as reaction solvents.

Both oligomers **IV** and **V** are less soluble than starting compounds. They are almost insoluble in organic solvents at room temperature and this leeds to problems with recording their NMR and UV-vis spectra. Studies of **IV** and **V** properties are in progress.

Experimental.

Oligomer IV. To the boiling solution of **I** (0.872g, 4mmol) in 400ml of 2,4-dichlorotoluene warm solution of **II** (0.2g, 1mmol) in 25ml of 2,4-dichlorotoluene was added dropwise during 10min and reaction mixture was heated at reflux 5hrs. Solvent was removed at rotatory evaporator with oil bath heating and residual crude **IV** was suspended in ethyl acetate, filtered, washed with ethyl acetate, and dried. The yield of **IV** was 0.391g (65%), yellow powder [3].

Oligomer V. To the boiling solution of **II** (0.801g, 4mmol) in 50 ml of 2,4-dichlorotoluene hot solution of **I** (0.218g, 1mmol) in 150ml of 2,4-dichlorotoluene was added dropwise at constant boiling during 15min, and reaction mixture was heated at reflux 5 hrs. Solvent was removed at rotatory evaporator with oil bath heating. Residual crude **V** was suspended in ethyl acetate, filtered, washed with ethyl acetate, and dried. The yield of **V** was 0.349g (60%), brownish yellow powder [4].

References.

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2. Wong, H. (Lokheed Martin Co.). Anti-contamination coated multi-layer insulation. **US 7252890** (428/626; B32B 15/08), 07.08.2007; appl. 10/790591, 01.03.2004. (*Chem. Abstr*. 2007, **147**:236312).

3. **IV**, MS, m/z(%): 600(M^+)(1), 570(1), 283(1), 198(1), 196(2), 194(1), 178(2), 177(1), 176(4), 175(3), 174(4), 173(2), 163(1), 162(5), 161(7), 160(8), 159(10), 149(6), 147(2), 146(1), 143(2), 141(9), 140(1), 139(3), 135(1), 127(7), 126(2), 125(28), 124(3), 123(5), 121(1), 115(1), 113(6), 112(2), 111(7), 110(2), 109(3), 102(2), 101(1), 99(3), 98(2), 97(3), 90(1), 89(11), 88(2), 87(4), 86(3), 85(4), 84(4), 83(2), 78(1), 77(13), 76(3), 75(9), 74(10), 73(9), 72(2), 71(1), 69(1), 65(1), 63(11), 62(10), 61(7), 60(4), 59(2), 57(3), 56(2), 55(4), 53(2), 52(3), 51(9), 50(10), 49(5), 48(2), 47(3), 45(3), 44(100), 43(12), 42(2), 41(6), 40(8), 39(11), 38(7), 37(10), 36(4), 35(5).
4. **V**, MS, m/z(%): 582(M^+)(1), 560(2), 537(1), 509(2), 460(4), 409(1), 398(2), 350(3), 311(1), 292(2), 250(2), 238(2), 231(3), 226(2), 200(10), 188(1), 162(1), 149(4), 138(2), 127(1), 126(1), 125(2), 108(12), 105(4), 104(1), 103(1), 102(5), 93(3), 92(2), 90(3), 81(1), 80(12), 79(1), 78(2), 77(7), 76(3), 74(3), 69(2), 67(2), 66(3), 65(12), 64(3), 63(3), 57(3), 56(2), 55(8), 54(3), 53(9), 52(9), 51(7), 50(6), 45(2), 44(100), 42(5), 41(18), 40(11), 39(16), 38(5), 37(5), 36(1).