High Perform. Polym. **11** (1999) 405–415. Printed in the UK PII: S0954-0083(99)08395-6

Low-temperature route to 1,2-benzoylenebenzimidazole ladder structure

D Likhatchev†, S Granados-Fócil†, R Gaviño‡, M Canseco† and L Alexandrova†

† Instituto de Investigaciones en Materiales, UNAM, Apdo. Postal 70-360, Deleg. Coyocan, 04510, Mexico

‡ Instituto de Quimica, UNAM, Apdo. Postal 70-360, Deleg. Coyocan, 04510, Mexico

E-mail: likhach@servidor.unam.mx

Received 2 August 1999, accepted for publication 30 September 1999

Abstract. Low-temperature catalytic conversion of *N*-(*o*-aminophenyl)phthalamic acid (**I**) was studied as a model reaction for the synthesis of ladder poly(aroylenebenzimidazole)s. The treatment of **I** with acetic anhydride/pyridine or trifluoroacetic anhydride resulted in the selective and quantitative cyclodehydration to yield either imide or isoimide structures respectively. The imidization was accompanied by acylation of the *ortho* amino group to form lateral acetamide or trifluoroacetamide substitutes. Thermodynamically unstable *N*-(*o*-trifluoroacetamidophenyl)phthalisoimide (**III**) underwent secondary cyclization to yield ladder 1,2-benzoylenebenzimidazole (**V**) between 130 and 150 °C. The conversion of this reaction did not exceed 35% because it competed with the thermal isomerization of **III** to the stable *N*-(*o*-trifluoroacetamido-phenyl)phthalimide (**IV**). The cyclization of *N*-(*o*-trifluoroacetamidophenyl)phthalisoimide (**III**) was found to be possible even at room temperature. The formation of 30–35% of the ladder 1,2-benzoylene-benzimidazole (**V**) was observed after **III** was dissolved in DMF and stored at room temperature for 4–10 h. This also was accompanied by the catalytic isoimide-to-imide isomerization. The obtained data may be useful for the further development of novel low-temperature approaches to the synthesis of ladder poly(aroylenebenzimidazole)s. Synthesis of aromatic polyimides and polyisoimides with lateral alkylamide or trifluoroalkylamide from available aromatic dianhydrides and tetraamines may also be of practical interest.

1. Introduction

Aroylenebenzimidazoles and aroyleneperinones resulting from the reaction of aromatic anhydrides and *ortho* diamines have been extensively studied since the early 1920s [1–13]. First, they gave rise to a variety of highly stable dyes [1–6] and, in the mid-1960s, this chemistry was successfully applied to the synthesis of heteroaromatic ladder polymers like polybenzoylenebenzimidazoles or polyimidazopyrrolones (pyrrones), polynaphthoylenebenzimidazoles and polybenzimidazobenzophenanthrolines (BBL). Low molecular weight prototypes like 1,2-benzoylenebenzimdazole were frequently used as model compounds to elucidate the complex mechanism for the formation of these polymers [7–13].

Nowadays, interest in the highly conjugated poly(aroylenebenzimidazole)s has been renewed, because in addition to their outstanding thermal and chemical resistance some of them were recently found to possess interesting nonlinear optical properties and electrical conductivity in the doped state. These make them promising candidates for the next generation

0954-0083/99/040405+11$30.00

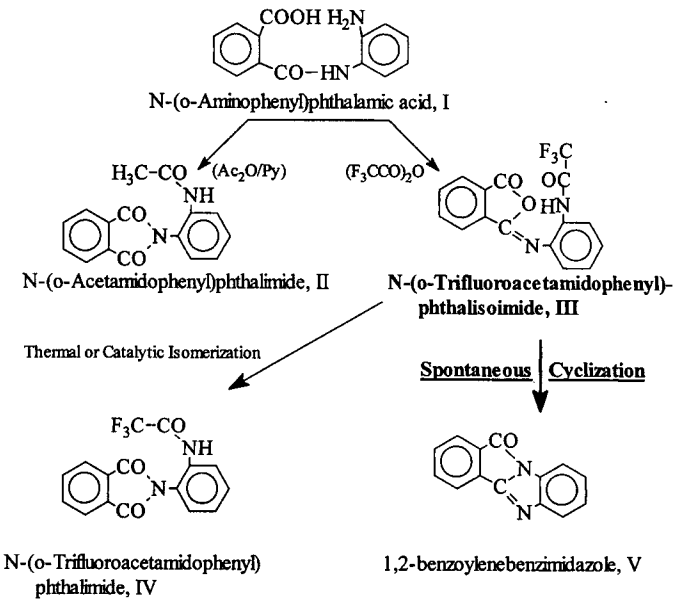
of micro- and optoelectronic devices [14, 15]. However, their practical use requires novel synthesis approaches providing a highly homogeneous chemical structure all along the macromolecular backbone. No progress has been made in this area since the late 1960s when conventional techniques such as thermal conversion of soluble precursor in the condensed state under 300–350 °C or direct polycondensation in polyphosphoric acid were developed. Both of these methods are inefficient to yield a polymer with well-defined chemical structure because of the numerous inherent drawbacks [13–16].

In the present work, the possibility of low-temperature synthesis of poly(aroylenebenzimidazole)s was studied by using a model reaction of the catalytic dehydration of *N*-(*o*-aminophenyl)phthalamic acid in the presence of acetic or trifluoroacetic anhydrides.

2. Experiment

2.1. Materials

All reagents were supplied by Aldrich Chemical, Co. Phthalic anhydride was crystallized from acetic anhydride and sublimated under vacuum and 1,2-diaminobenzene was crystallized repetitively from ethanol prior to use. The rest of the reagents and solvents were used as-received.



Scheme 1.

2.2. Synthesis of N-(o-aminophenyl)phthalamic acid (I).

Phthalic anhydride (14.8 g, 0.10 mol) was added to the solution of 1,2-diaminobenzene (10.8 g, 0.10 mol) in 70 ml of THF. The reaction mixture was stirred for 4 h at room temperature. Then, **I** was separated as a white precipitate by filtration and dried under vacuum to a constant weight. The conversion was above 90%, m.p. 151 °C (lit. [8, 10] m.p. 147–152 °C). The FTIR and NMR spectra completely corresponded to the data recently reported elsewhere [13].

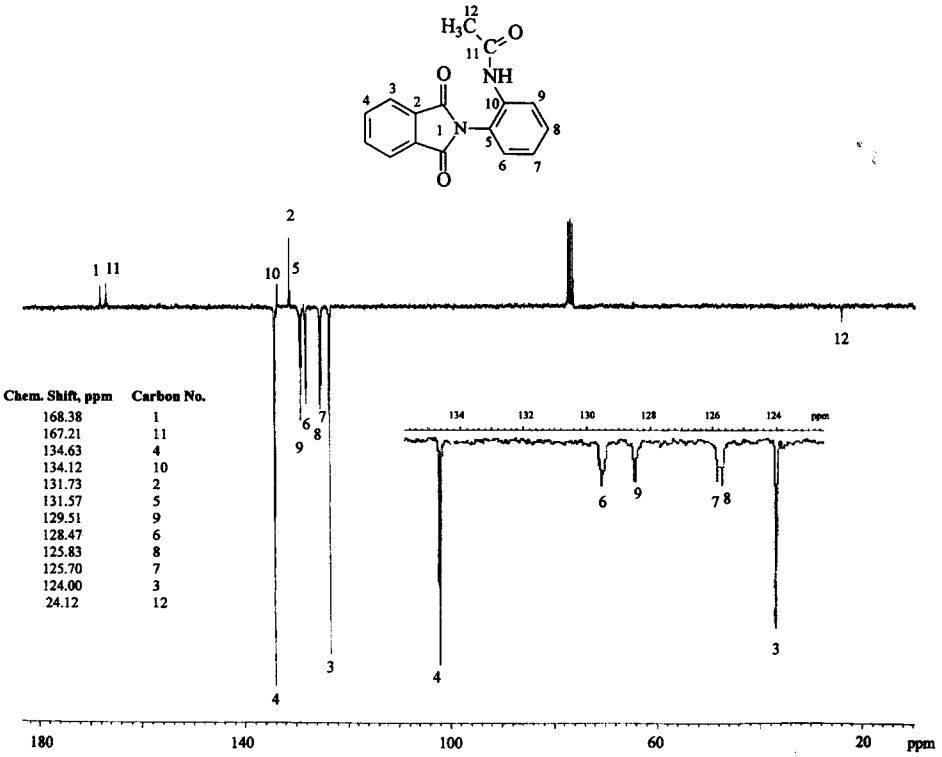


Figure 1. APT-NMR spectrum of *N*-(*o*-acetamidophenyl)phthalimide, **II** (solution in $CDCl_3$).

2.3. Catalytic conversion of N-(o-aminophenyl)phthalamic acid (I).

Catalytic cyclodehydration of **I** was performed as shown in scheme 1. Dry powder of **I** (10 g) was treated with 100 ml of the mixture of acetic anhydride and pyridine (50/50 by volume). The reaction mixture was stirred for 10 h at room temperature and then poured into water to yield *N*-(*o*-acetamidophenyl)phthalimide (**II**).

The product was crystallized from ethanol and dried to constant weight under vacuum. The obtained white crystals had m.p. 199 °C; ^{13}C NMR (see figure 1) ($CDCl_3$): δ = 168.38 (1, CO imide), 167.21 (11, CO amide), 134.63 (4), 134.12 (10), 131.73 (2), 131.57 (5), 129.51 (9), 128.47 (6), 125.83 (8), 125.70 (7), 124.00 (3), 24.12 (12) ppm; FTIR (see figure 2): 3335 (amide NH), 1782, 1765, 1721, 1707 (CO imide-1), 1682 (amide-1), 1532 (amide-2), 1383 (CNC imide-2), 1111 (CNC imide-3), 723 (imide-4) cm^{-1}. EI-MS m/z (rel. int. %): 280 (82, M^+), 238 (77, $M^+ - 42$, $C_{14}H_{10}N_2O_2$), 220 (48, $M^+ - 60$, $C_{14}H_8N_2O$), 194 (100, $M^+ - 86$, $C_{13}H_{10}N_2$). Elemental analysis (found: C 68.63%, H 4.29%, N 10.03%; calculated: C 68.57%, H 4.32%, N 9.99%).

N-(*o*-trifluoroacetamidophenyl)phthalisoimide (**III**) (see structure in scheme 1), was obtained by stirring solid **I** (10 g) in 50 ml of trifluoroacetic anhydride for 10 h at room temperature. The resulting product was filtered off, crystallized from ethyl ether and dried to constant weight under vacuum at room temperature. The pale yellow needle-shaped crystals produced in this manner had m.p. 150 °C at a heating rate of 5 °C min^{-1}. The APT-NMR and FTIR spectra of **III** are shown in figures 3 and 4 respectively. Elemental analysis (found: C 57.56%, H 2.92%, N 8.31%; calculated C 57.49%, H 2.71%, N 8.38%).

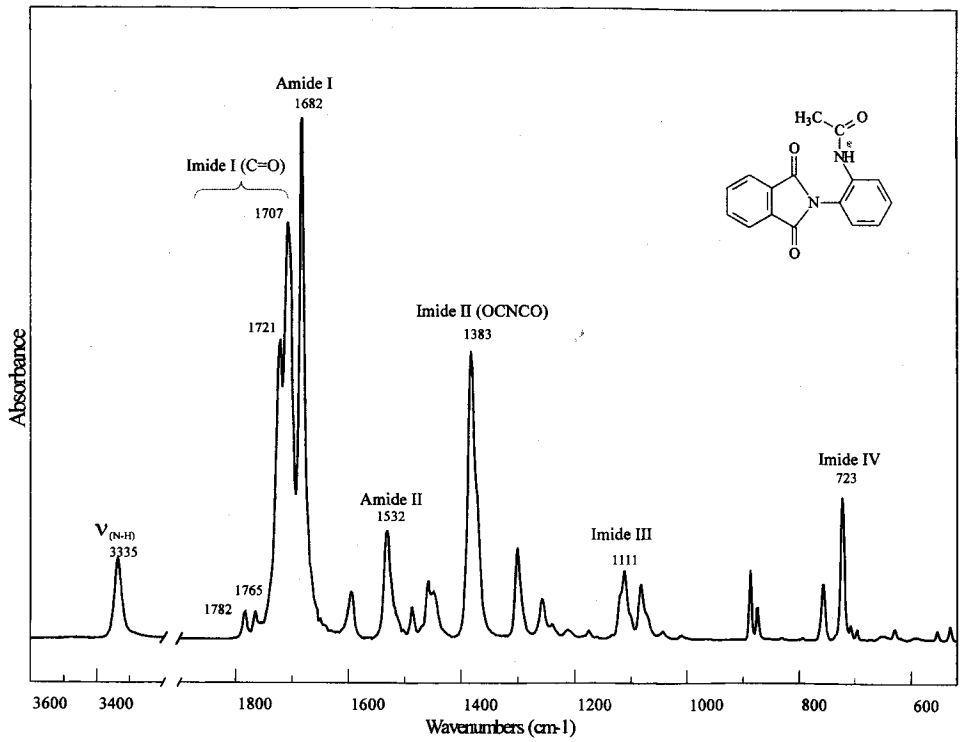


Figure 2. FTIR spectrum of *N*-(*o*-acetamidophenyl)phthalimide, **II**.

N-(*o*-trifluoroacetamidophenyl)phthalimide (**IV**) resulted from catalytic isomerization of **III** in excessive amounts of *N*, *N*, *N'*, *N'*-tetramethylethylenediamine during 20 h at room temperature. White needle-shaped crystals of **IV** were filtered off, crystallized from ethanol and dried to constant weight under vacuum: m.p. 236 °C, ^{13}C NMR (see figure 5) ($CDCl_3$): 165.47 (1, CO imide), 154.04 (11, $^2J^{C-F}$ = 37 Hz), 133.39 (4), 131.47 (2), 131.18 (10), 128.41 (6), 128.13 (9), 126.21 (8), 125.80 (7), 125.13 (5), 122.44 (3), 115.87 (12), $^1J^{C-F}$ = 289 Hz); FTIR (see figure 6): 3275 (amide NH), 1786, 1767, 1728, 1713 (CO imide-1), 1697 (amide-1), 1541 (amide-2), 1390 (CNC imide-2), 1251, 1167, 1142 (C-F), 1116 (CNC imide-3), 715 (imide-4). EI-MS m/z (rel. int. %): 334 (100, M^+), 265 (58, $M^+ - 69$, $C_{15}H_9N_2O_3$), 221 (72, $M^+ - 113$, $C_{14}H_8N_2O + 1$). Elemental analysis (found: C 56.69%, H 2.69%, 8.51%; calculated: 57.49%, H 2.71%, N 8.38%).

The synthesis of 1,2-benzoylenebenzimidazole, (**V**), has been described in detail elsewhere [13], m.p. 214 °C (lit. [8, 10] m.p. 215 °C). The APT-NMR spectrum is shown in figure 7. EI-MS m/z (rel. int. %): 220(100, M^+), 192(14, $M^+ - 28$), 164 (7, $M^+ - 56$). Elemental analysis (found: C 75.98%, H 3.74%, N 13.01%; calculated: C 76.35%, H 3.66%, N 12.72%.

2.4. Measurements

The FTIR and NMR (^1H: 300 MHz and ^{13}C: 75 MHz) spectra were recorded using Nicolet 510P and Varian Unity 300 spectrometers respectively. ^1H–^1H COSY and HETCOR spectra were used for assignment for all proton resonance and an LRHETCOR [17], where the

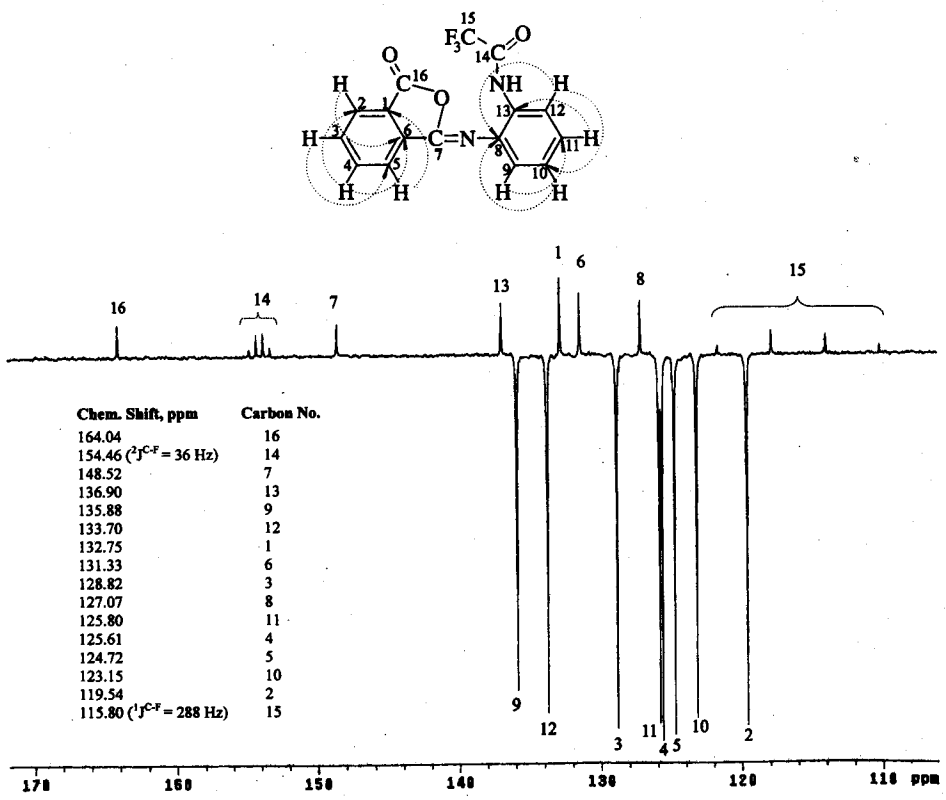


Figure 3. APT-NMR spectrum of *N*-(*o*-trifluoroacetamidophenyl)phthalisoimide, **III** (solution in $CDCl_3$).

duration of the fixed delay in the operator ($\tau - 9.5$ Hz), was used for assignment of all carbon resonances as shown in figures 3 and 7.

A Du Pont, high-resolution thermogravimetric analyser, TGA 2950, was used for the thermal analysis at a heating rate of 5 °C min^{-1}, and DSC measurements were done using a T.A. Instruments differential scanning calorimeter, Model 2100.

Mass spectra (EI-MS) were obtained on a Jeol JMS-SX 102 mass spectrometer using a 70 eV electron impact ion source.

3. Results and discussion

Catalytic cyclodehydration of *N*-phenylphthalamic acid was studied in the mid-1960s [18, 19]. The direction of this reaction was shown to depend on the acidity of the dehydration agent and the presence of catalysts. Moderately acidic acetic anhydride in combination with tertiary amines leads to the normal imide structure while an isomeric iminolactone (isoimide) cycle usually forms in the highly acidic trifluoroacetic anhydride. These data were later successfully used for the development of the low-temperature catalytic conversion (chemical imidization) of aromatic poly(amic acid)s to polyimides.

An attempt at catalytic cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid at low-temperature was undertaken for the first time in the present work. Bibliographic analysis

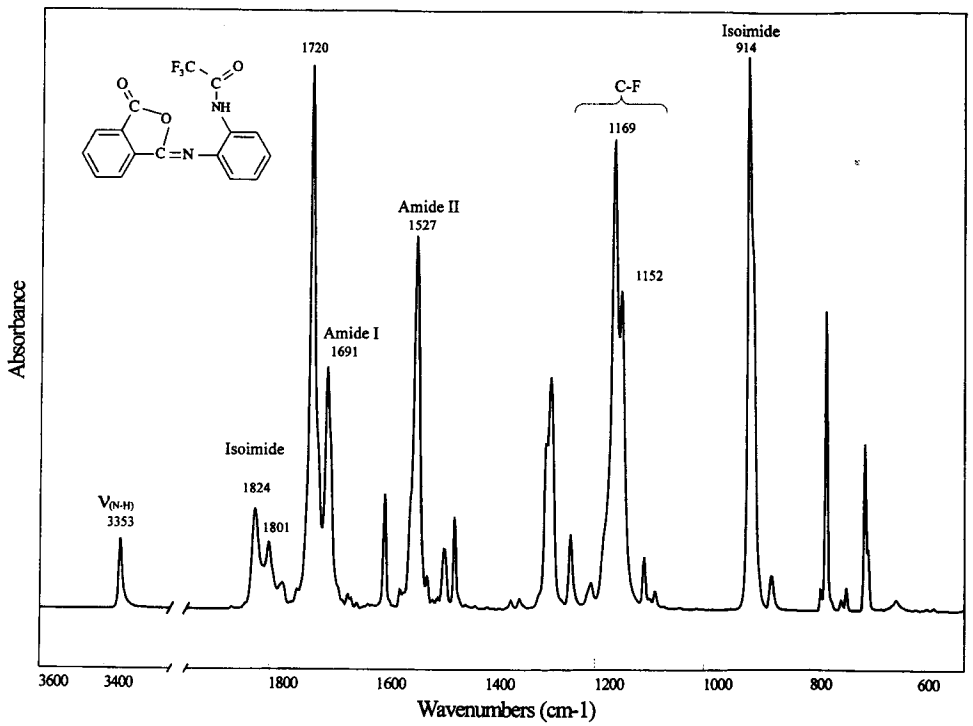


Figure 4. FTIR spectrum of *N*-(*o*-trifluoroacetamidophenyl)phthalisoimide, **III**.

indicates that in all previous studies **I** was converted to 1,2-benzoylenebenzimidazole via high-temperature treatment in melt or in refluxing solvents above 90 °C [1–13]. Both these routes are complicated by the formation of various intermediates and by-products that, in the case of the corresponding polymers, would lead to an indefinite chemical structure [7, 8, 10, 11, 13].

Low-temperature catalytic treatment of **I** with acetic anhydride/pyridine or trifluoroacetic anhydride led to the selective and quantitative conversion to the imide and isoimide structures, respectively (see scheme 1), which is in agreement with the previous results for *N*-phenylphthalamic acid [18, 19]. The only, but important, difference that resulted from the presence of a free *ortho* amino group in the diamine moiety was its quantitative acylation during the cyclodehydration process to form lateral acetamide or trifluoroacetamide. The APT-NMR and FTIR spectra of the isoimide **III** are presented in figures 3 and 4. The latter clearly shows the characteristic iminolactone modes at 1824, 1801 and 914 cm^{-1} and amide bands at 3353 (N-H stretching), 1691 (amide-1), 1527 (amide-2) and very strong multiple band at 1169–1152 cm^{-1} (C-F stretching). These are supported by the probable assignment of the APT-NMR signals presented in figure 3.

The FTIR spectra of imide **II** (figure 2) resembled those reported for the substituted *N*-phenylphthalimides [13, 20]. The main feature of these spectra may be the splitting of the imide carbonyl mode to four peaks, instead of two expected (symmetric and asymmetric C=O stretching), which is due to the Fermi resonance arising through the interaction of the fundamental carbonyl band and the overtone of Ar–CO mode around 875 cm^{-1} [20]. The differences between FTIR patterns of **II** and non-substituted *N*-phenylphthalimide [20] include the presence of acetamide bands at 3335 (amide N-H stretching), 1682 (amide-1), and 1532 (amide-2) in the former spectrum. These correspond well to the results of APT-NMR analysis (see figure 1).

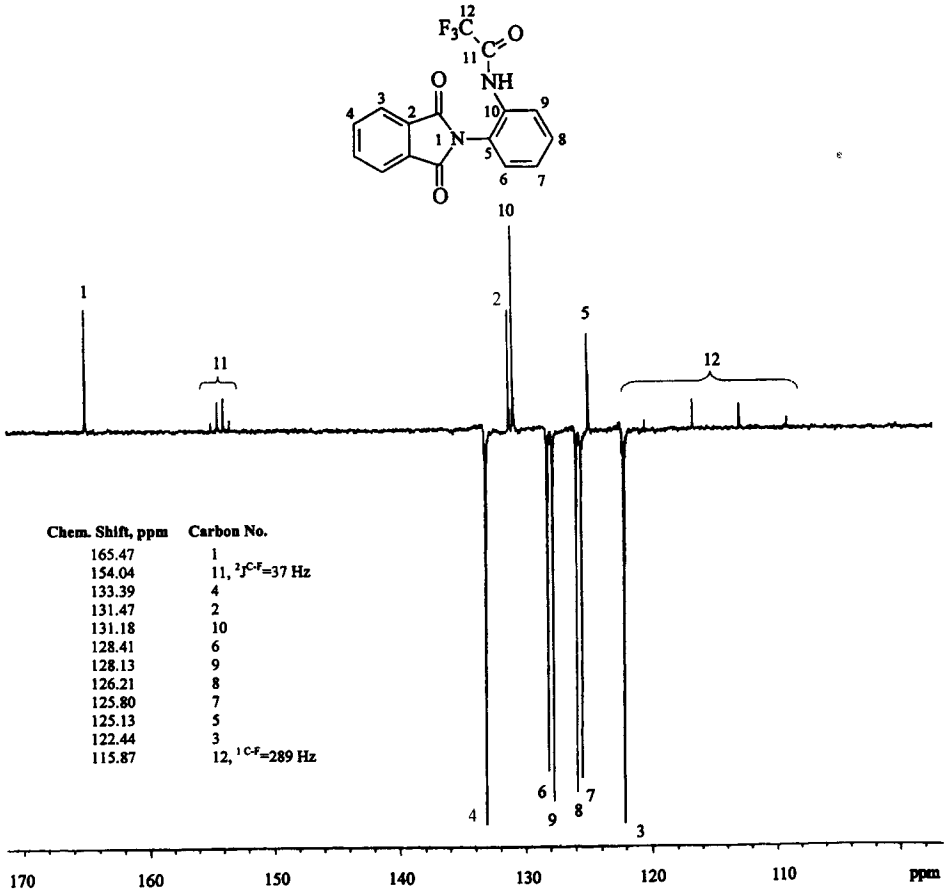


Figure 5. APT-NMR spectrum of *N*-(*o*-trifluoroacetamidophenyl)phthalimide, **IV** (solution in $CDCl_3$).

In basic media like pyridine or *N*, *N*, *N'*, *N'*-tetramethylethylenediamine, isoimide **III** underwent quantitative isomerization to *N*-(*o*-trifluoroacetamidophenyl)phthalimide (**IV**). Both FTIR and APT-NMR spectra indicated complete isoimide-to-imide conversion after 20 h of treatment at room temperature. Newly formed compound **IV** preserved the lateral trifluoroacetamide group in the diamine moiety (see figures 5 and 6). The imides **II** and **IV** demonstrated good thermal stability. Their thermal (TGA and DSC) and spectral analysis indicated no sign of any decomposition or chemical transformation up to the well defined melting temperatures at 199 °C and 236 °C, respectively.

In contrast to these, isoimide **III** started to lose weight at 129 °C with the deflection point on the slope at 155 °C when it was heated at 5 °C min^{-1} (see figure 8). The DSC tests showed that this was accompanied by the appearance of a strong exothermic peak at 151 °C following the melting endotherm at 150 °C. The leaving product was collected using a sealed vacuum system connected to the tube cooled by liquid nitrogen. This was identified as trifluoroacetic acid. The FTIR and NMR spectra of the resulting solids indicated the presence of 1,2-benzoylenebezimidazole (**V**) (see APT-NMR spectrum in figure 7), and *N*-(*o*-trifluoroacetamido-phenyl)phthalimide (**IV**). Partial separation of these structures in the form

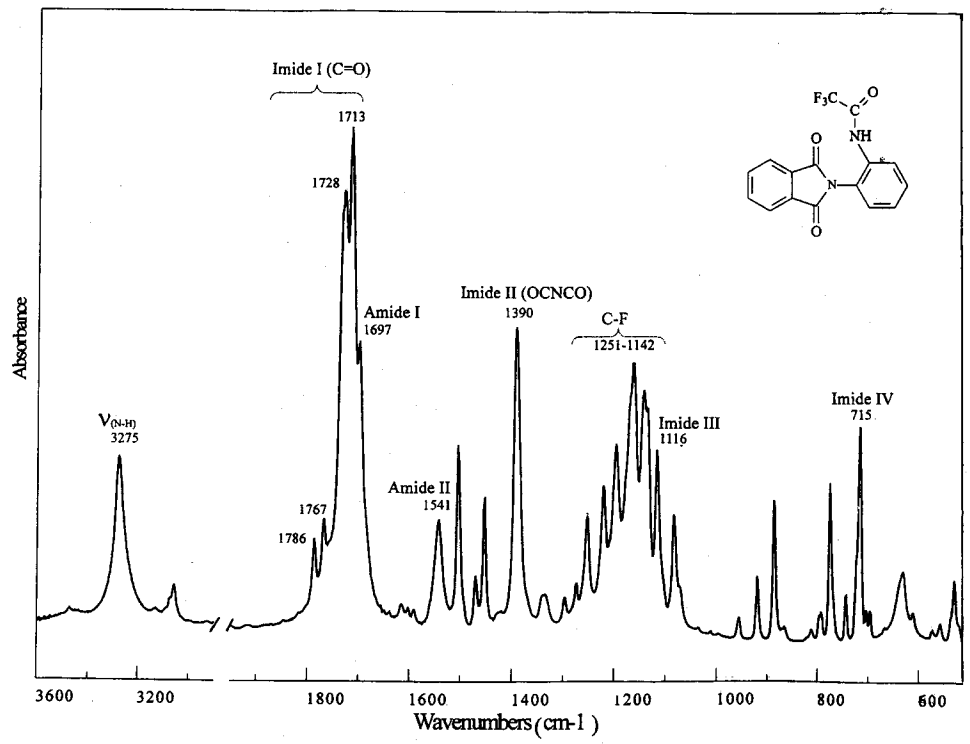


Figure 6. FTIR spectrum of *N*-(*o*-trifluoroacetamidophenyl)phthalimide, IV.

of yellow (**V**) and white (**IV**) crystals occurred in the reaction system above 180 °C due to the sublimation followed by the precipitation of the products in the different zones of the tube.

The obtained results demonstrate that there are at least two competitive reactions during thermal treatment of isoimide **III** leading to either the isomerization to the imide structure **IV** or secondary cyclization to 1,2-benzoylenebenzimidazole **V** via elimination of trifluoroacetic acid. The ratio of the resulting products was controlled by the heating rate. Slower heating favoured the formation of **V** but even at 0.5 °C min^{-1} its concentration in the final mixture was no more than 30–40%. It is important to note that *N*-(*o*-trifluoro-acetamidophenyl)phthalisoimide **III** converts to the ladder 1,2-benzoylenebenzimidazole **V** at remarkably lower temperatures than the main intermediates of the conventional thermal cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid **I**, namely *N*-(*o*-aminophenyl)phthalimide (above 190 °C) or 2-(*o*-carboxy-phenyl)benzimidazole (above 250 °C) [8, 10, 13]. This appears to be due to the known thermodynamic instability of the isoimide structure and high efficiency of trifluoroacetic acid as a leaving group.

The formation of the ladder 1,2-benzoylenebenzimidazole was found to be possible even at room temperature. Precipitation of the yellow needle-shaped crystals of **V** was observed 5–6 h after a DMF solution of **I** (10 wt%) was diluted with an equal volume of trifluoroacetic anhydride. The conversion was about 35% and did not increase when the experiment was repeated at elevated temperatures up to 60 °C. Mother liquid resulting from the separation of the precipitate was poured into water to yield isoimide **III** with slight traces of **V**.

To ensure the role of the isoimide **III** as an intermediate in the low-temperature route to **V**, the former was dissolved in DMF (10 wt%). This reaction afforded 27% of

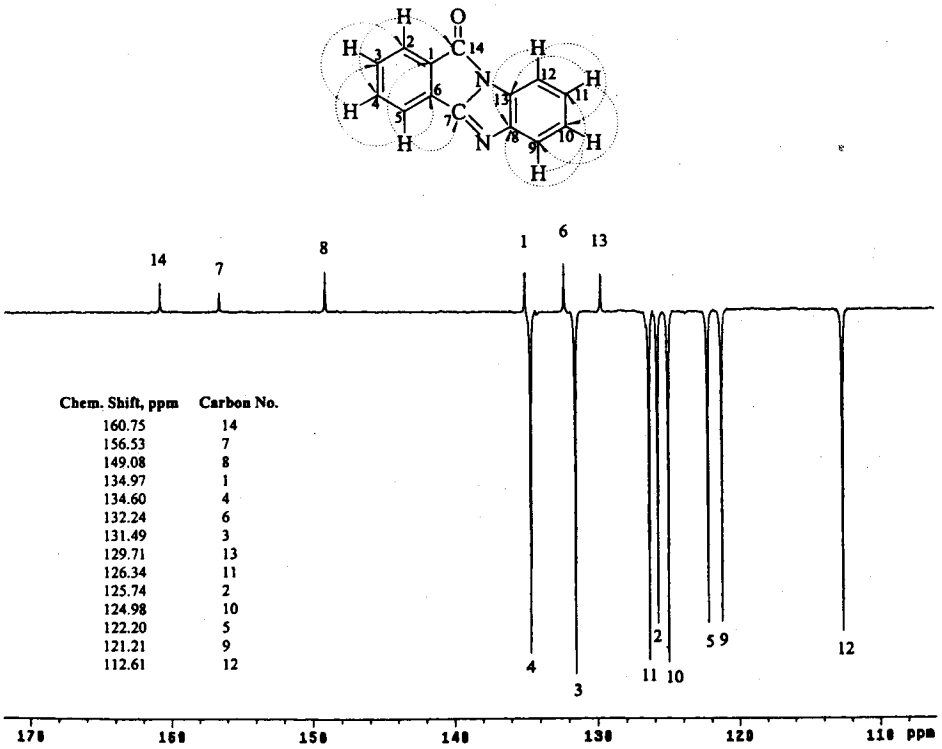


Figure 7. APT-NMR spectrum of 1,2-benzoylenebezimidazole, **V** (solution in $CDCl_3$).

1,2-benzoylenebenzimidazole **V** and 73% of *N*-(*o*-trifluoroacetamidophenyl)phthalimide **IV** after 48 h storage at room temperature. Ladder 1,2-benzoylenebenzimidazole precipitated from the solution while imide **IV** was recovered by pouring the mother liquid into water. It is apparent that the formation of **V** competes with the isomerization of isoimide **III** yielding thermodynamically favourable *N*-(*o*-trifluoroacetamidophenyl)phthalimide **IV**. The rate of the isomerization process increased dramatically when more basic solvents like pyridine or *N*, *N*, *N'*, *N'*-tetramethylethylenediamine were used as the reaction media, meanwhile in pure highly acidic trifluoroacetic anhydride isoimide **III** remained stable for weeks. No formation of the ladder 1,2-benzoylnebenzimidazole was observed in these cases.

4. Conclusions

The possibility of a low-temperature synthesis for the ladder 1,2-benzoylnebenzimidazole was studied by means of catalytic cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid **I** in the presence of acetic anhydride/pyridine or trifluoroacetic anhydride. This treatment was found to lead to the selective and quantitative conversion of **I** to imide **II** or isoimide **III** respectively, and was accompanied by acylation of the *ortho* amino group to yield lateral acetamide or trifluoroacetamide groups in the diamine moiety. Thermal treatment of *N*-(*o*-trifluroacetamidophenyl)phthalisoimide **III** at a heating rate below 5 °C min^{-1} resulted in both the formation of 1,2-benzoylenebenzimidazole **V** at 130–150 °C and thermal isomerization to *N*-(*o*-trifluoro-acetamidophenyl)phthalimide **IV**. The same products **IV** and **V** were obtained

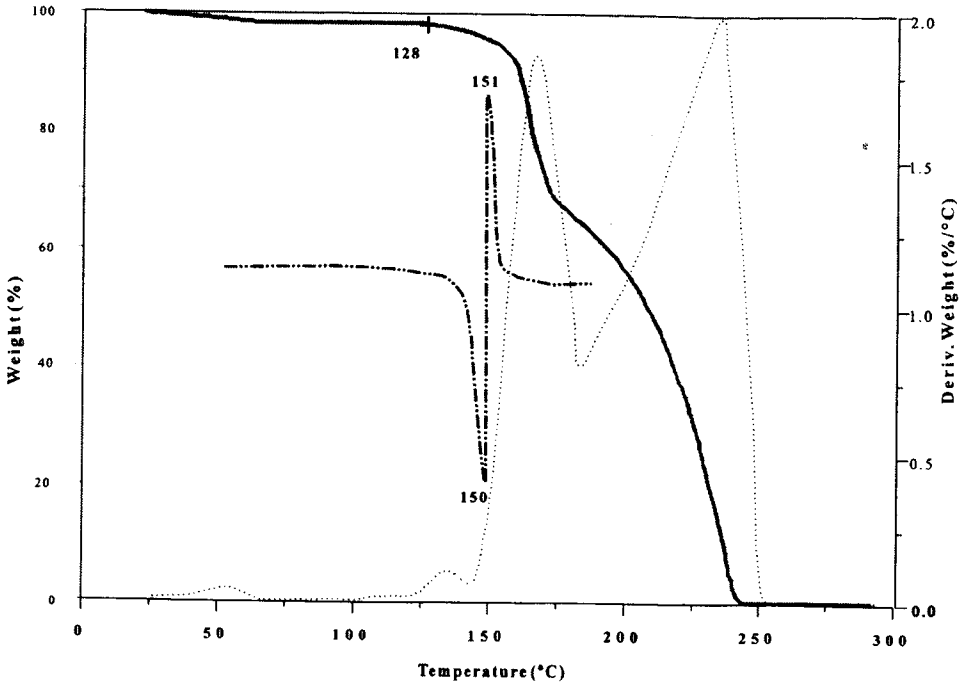


Figure 8. TGA (——, weight loss; ·····, derivative) and DSC (— · · —) curves of *N*-(*o*-trifluoroacetamidophenyl)phthalisoimide, **III**.

when isoimide **III** was dissolved in DMF and stored at room temperature. The conversion to **V** was below 35%. The obtained data may be useful for the development of novel low-temperature synthesis routes to heteroaromatic ladder polymers like polybenzoylenebenzimidazoles and polybenzimidazobenzophenanthrolines with well-defined chemical structure. Synthesis of aromatic polyimides and polyisoimides with lateral alkylamide or trifluoroalkylamide from available aromatic dianhydrides and tetraamines may also be of particular interest.

Acknowledgments

The authors would like to acknowledge Javier Perez-Flores MSc and Carmen Vázquez-Ramón MSc for their valuable assistance in mass spectrometry and thermal analysis studies.

References

[1] Bistrzycki A and Lecco A 1921 *Helv. Chim. Acta* **4** 425
[2] Chakravarti G C 1924 *Q. J. Ind. Chem. Soc.* **1** 19
[3] Bistrzycki A and Risi J 1925 *Helv. Chim. Acta* **8** 810
[4] Okazaki M 1955 *J. Soc. Org. Synth. Chem., Japan* **13** 80
[5] Krasovitskiĭ B M, Matskevich R M, Radochina N A and Ryazanova K P 1958 *Zhur. Obschei Khim.* **28** 2485
[6] Arient J and Marahan J 1961 *Coll. Czech. Chem. Comm.* **26** 2774
[7] Dawans F and Marvel C S 1965 *J. Polym. Sci. Part A* **3** 3549
[8] Colson G, Michel R H and Paufler R M 1966 *J. Polym. Sci. Part A* **4** 59
[9] Paudler W and Zeiler A G 1969 *J. Org. Chem.* **34** 2138
[10] Young R 1972 *J. Heterocyclic Chem.* **9** 371

[11] Young R 1973 *J. Heterocyclic Chem.* **10** 325
[12] Korshak V V, Rusanov A L, Pavlova S A, Gribkova P N, Mikadze L A, Bochvar D A, Stankevich T V and Tomilin O B 1975 *Dokl. Akad. Nauk. SSSR* **261** 1334
[13] Likhatchev D, Valle L, Canseco M, Salcedo R, Gabiño R, Martinez-Richa A, Alexandrova L and Vera-Graziano R 1998 *J. Appl. Polym. Sci.* **67** 609
[14] Wang C S 1993 *Trends Polym. Sci.* **1** 199
[15] Wang C S and Dorton M 1996 *Polymeric Materials Encyclopedia* 1st edn, vol 2 (Boca Raton, FL: CRC Press) pp 1461–72
[16] Bailey W J 1988 *Encyclopedia of Polymer Science and Engineering* 2nd edn, index vol (New York: Wiley) pp 158–95
[17] Salazar M, Zektzer A S and Martin G E 1988 *Magn. Res. Chem.* **26** 28
[18] Ernst M L and Schinir J L 1966 *J. Am. Chem. Soc.* **88** 5001
[19] Sauers C K, Marikakis C A and Lupton M A 1972 *J. Am. Chem. Soc.* **94** 8156
[20] Kardash I Ye, Likhatchev D Yu, Krotovich M B, Zhuravleva I L, Bogachev Yu S, Kozlova N V and Pravednikov A N 1987 *Polym. Sci. USSR* **29** 1498