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Synthesis and identification of dinitro- and diamino-terephthalic acid

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Abstract

Dinitroterephthalic acid (DNTPA) and diaminoterephthalic acid (DATPA) were prepared in 85% and 75% yields, respectively. These compounds were characterized by using FTIR and ^{1}HNMR. DATPA can be used as a monomer for the preparation of polyesters and polyamides.

Keywords: Terephthalic acid; Dinitroterephthalic acid; Diaminoterephthalic acid

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The aromatic ring of terephthalic acid is highly deactivated toward electrophilic substitution. However, scattered references are found in the literature for its reaction with inorganic species [1]. Nitration provides a route to nitroterephthalic acid, and, while terephthalic acid is remarkably stable to sulfonation in the absence of a catalyst, it reacts with sulfuric acid in the presence of mercuric salts to give sulfoterephthalic acid (1). Chlorination leads to the commercially important dimethyltetrachloroterephthalate,“Dachthal”. In spite of these references, no substitution of terephthalic acid with an electron-deficient carbon species has been observed. Attaching substituents of variable structure to the main chain of a polymer may be done with different purposes such as to affect the solubility, clarity, melting or to introduce functional groups which allow cross-linking. A series of electron acceptor polyesters was prepared from 5-nitroisophthalic, nitroterephthalic, and 4,6-dinitroisophthalic acids. Those polymers prepared at high molecular weight were tough, soluble, linear materials of well-defined structure. These materials were mixed with electron-donor polymers based on aryliminodiethanols where the aryl groups was phenyl, p-anisyl, 2,5-dimethoxyphenyl, and 3,4,5-trimethoxyphenyl. The effects of the mixtures on the mechanical, spectral, viscometric, and conductive properties were studied and compared to the component polymers [2–6].

The object of this work is to prepare diaminoterephthalic acid (DATPA) which our literature search showed that has not been prepared before. DATPA can be a useful monomer for preparation of polyamides or polyesters and it can also be used in resin production.

1. Experimental

All chemicals such as terephthalic acid, nitric acid, sulfuric acid, ethanol, Fe powder, hydrochloride acid, sodium bicarbonate were purchased either from Fluka or Merck Chemical Co.

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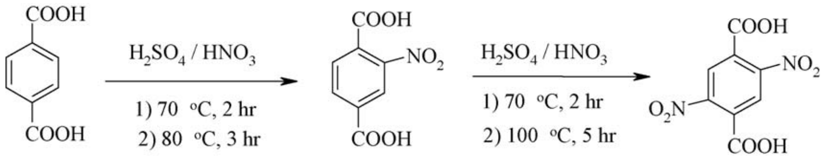
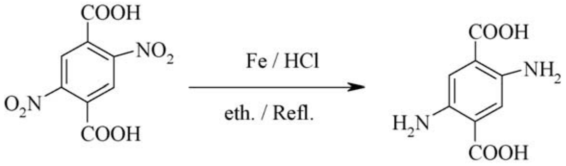


Scheme 1.



Scheme 2.

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The ^{1}H NMR spectra were recorded in DMSO-d_6 solution using a Bruker Advance DPX 500 MHz (GmbH, Germany).

MNTPA and DNTPA were prepared according to general procedure given in the literature [7] and that has been modified, Scheme 1. A 500-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer, decanter and condenser was charged with 20.7 g terephthalic acid. A mixture of 25 mL conc. sulfuric acid and 75 mL conc. nitric acid was added drop wise that caused the temperature raised to 80 °C. After the addition was complete, the reaction was continued at 100 °C for 3 h. To the suspension, another mixture of 25 mL conc. sulfuric acid and 100 mL conc. nitric acid was added drop wise while the temperature remained at 100 °C. After the complete addition, the reaction continued at 80 °C for 12 h. The reaction mixture was then put on water/ice mixture. The precipitate was filtered and the filtrate was dissolved in hot water to be recrystalized in the refrigerator. The formed crystal was filtered and dried in the oven at 50 °C. The melting point was 245 °C and the yield 85%.

We have used the general procedure for the reduction of nitro group given in the literature [8], Scheme 2. A 250-mL, three-necked, round-bottomed flask containing 9 g of iron powder, 15 mL of ethanol, 15 mL of water and 0.5 mL fuming hydrochloric acid. The flask was fitted with a mechanical stirrer, a reflux condenser and a thermometer. The mixture was heated to reflux with stirring for 10 min, then 3.2 g of DNTPA was added gradually over 20 min. After all the DNTPA was added, stirring was continued for another 10 min at reflux. Then the mixture was cooled down to room

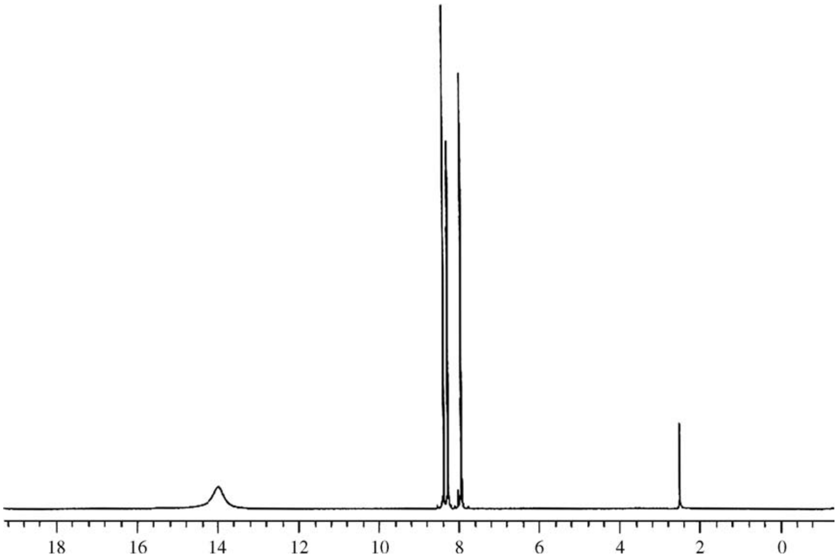


Fig. 1. ^{1}HNMR of MNTPA.

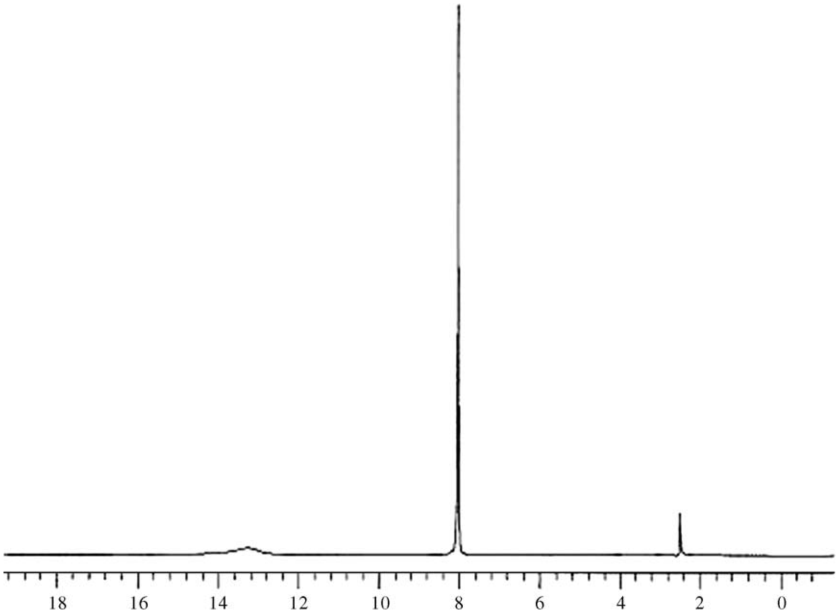


Fig. 2. ^{1}HNMR of DNTPA.

temperature and 0.3 g of sodium bicarbonate was added. After 3 h stirring, the mixture was filtered and the filtrate was concentrated by vacuum distillation. The residue was dissolved in absolute ethanol and the stoichiometric amount of 36% HCl was added and the mixture was heated to reflux with stirring for 1 h. Then the mixture was cooled down to room temperature and filtered. The solution under the filter was kept in a refrigerator to precipitate. The precipitate was filtered and dried in an oven at 50 °C for 24 h. It was purified by recrystallization from ethanol to give a pale light brown solid. Yield (75%): m.p.: 289 °C. IR (KBr, cm^{-1}): 3510, 3400 (N–H stretching), 1675 (s), 1600 (N–H deformation). ^{1}H NMR (DMSO-d$_6$, δ ppm): 8.1–7.3 (m).

2. Results and discussion

MNTPA and DNTPA were prepared using different times, temperatures and concentrations of sulfuric and nitric acid mixtures. TPA can accept only two nitro groups, so in low concentrations of acid mixtures, especially when nitric

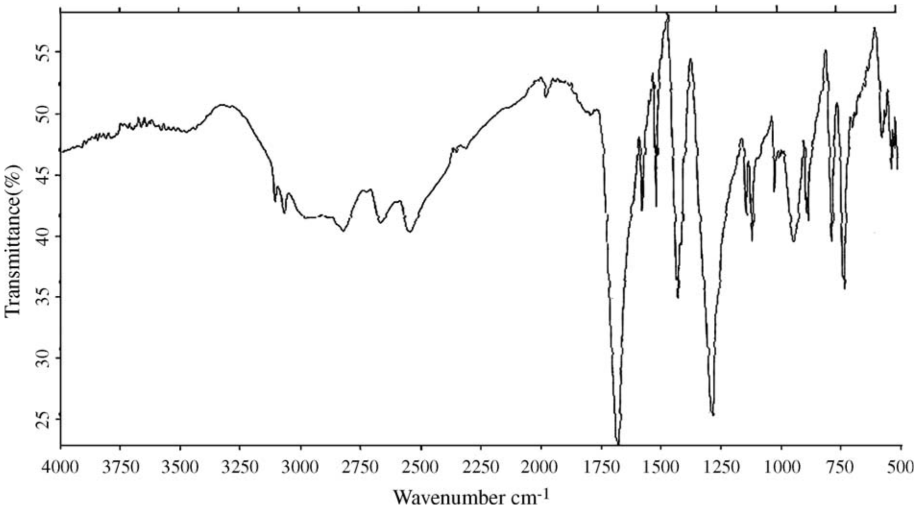


Fig. 3. IR spectra of DNTPA.

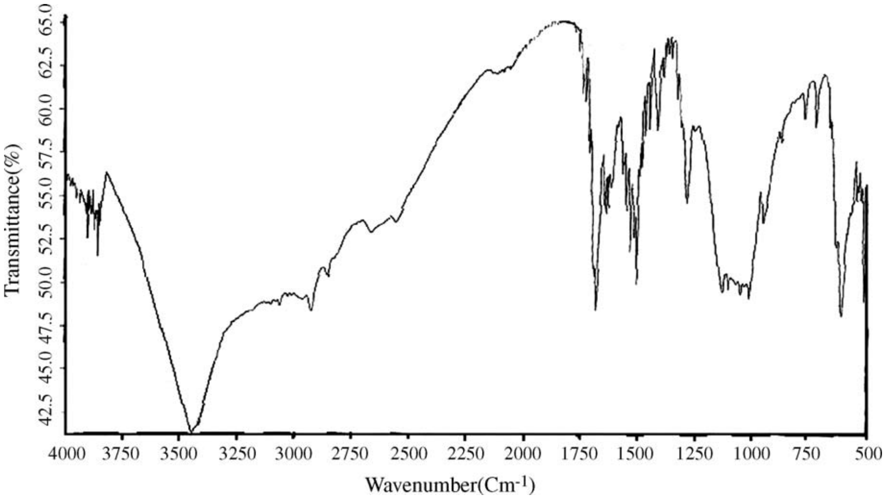


Fig. 4. IR spectra of DATPA.

acid is in lower concentration than sulfuric acid, formation of DNTPA is not possible and only MNTPA is prepared. To prepare DNTPA one can use higher concentrations of mixed acids at higher temperatures and longer times. Identification of these two compounds (MNTPA and DNTPA) were followed by their melting points (250 and 245 °C, respectively), ^{1}HNMR, and their solubility in hot water. One of the best methods for discrimination is ^{1}HNMR spectra. In ^{1}HNMR spectra of TPA, because of symmetry of all aromatic hydrogens, one can see only a singlet at about 8 ppm and acidic hydrogen at about 14 ppm. ^{1}HNMR spectra of MNTPA Fig. 1, showed a singlet signal at about 14 ppm and three other aromatic hydrogens in three different positions in the region of 8–8.5 ppm.

DNTPA compound showed a singlet signal at about 8 ppm due to symmetrical aromatic protons and one signal for acidic hydrogen at about 14 ppm, Fig. 2.

Comparison of IR spectra of DNTPA with that of TPA showed signals at 1485–1570 and 1320–1380 cm^{-1} regions related to nitrogroups.

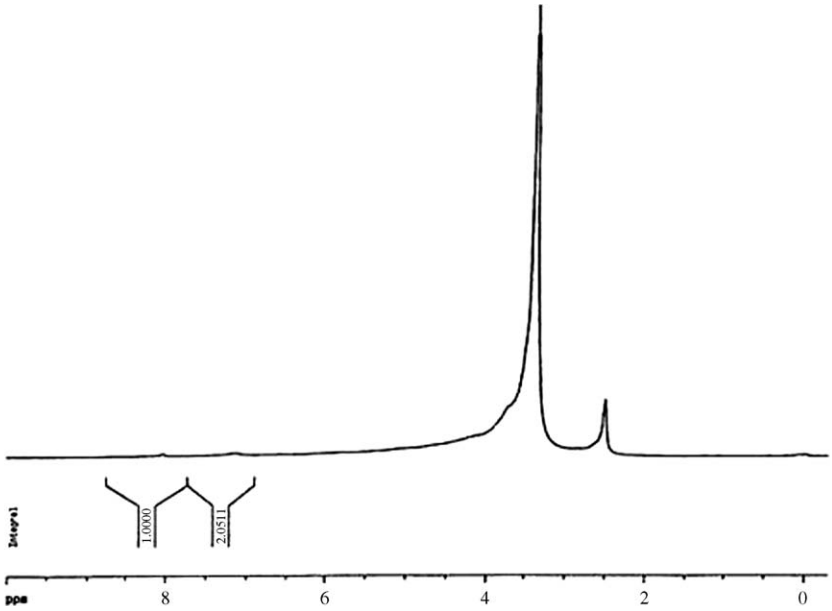


Fig. 5. ^{1}HNMR of DATPA.

The solubility of TPA, MNTPA and DNTPA were also examined in hot water. The results showed that DNTPA was soluble in hot water while TPA and MNTPA were not soluble in hot water at same conditions.

There are different ways to reduce nitrogroups to amine groups, here we have used the procedure given in the literature [8] using Fe powder and hydrochloric acid in ethanol at reflux for 80 min. The yield for DATPA was 75% and it was characterized by using FTIR and ^{1}HNMR. Comparison of IR spectra of DNTPA and DATPA in Figs. 3 and 4 show a sharp strong peak in the region of 3400 cm^{-1} in the IR spectrum of DATPA which is related to the absorption of $-NH_2$ group.

Comparison of ^{1}HNMR spectra of DNTPA and DATPA in Figs. 2 and 5 clearly shows the difference in the signal at the region of 7.3 ppm which is related to amine ($-NH_2$) group.

3. Conclusion

From the reactions and the related spectra of the prepared compounds, it was confirmed that DNTPA and DATPA can be prepared in a relatively high yields. The obtained compounds were characterized by FTIR, HNMR, solubility, and melting points.

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