

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis and Characterization of Phthalonitrile-Capped Phthalimido Anhydrides

Alka D. Gupta^a; Devendra Kumar^{bc}

^a Department of Chemical Engineering, Indian Institute of Technology, New Delhi, India ^b Centre for Material Science and Technology, Indian Institute of Technology, Hauz Khas, New Delhi, India ^c Polymeric Materials Division, Langley Research Center, Hampton, Virginia

To cite this Article Gupta, Alka D. and Kumar, Devendra(1986) 'Synthesis and Characterization of Phthalonitrile-Capped Phthalimido Anhydrides', *Journal of Macromolecular Science, Part A*, 23: 12, 1397 – 1414

To link to this Article: DOI: 10.1080/00222338608081132

URL: <http://dx.doi.org/10.1080/00222338608081132>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of Phthalonitrile-Capped Phthalimido Anhydrides

ALKA D. GUPTA

Department of Chemical Engineering
Indian Institute of Technology
New Delhi 110016, India

DEVENDRA KUMAR*

Centre for Material Science and Technology
Indian Institute of Technology
Hauz Khas, New Delhi 110016, India

ABSTRACT

The condensation in an aprotic solvent of 4-aminophthalonitrile with hexafluoroisopropylidenediphthalic anhydride (6FA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPTDA), 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), and bisester anhydride (BEA), respectively, gave the corresponding phthalamic acids. These phthalamic acids were thermally cyclodehydrated to give phthalonitrile-capped phthalimido anhydrides. Elemental analysis, differential thermal analysis (DSC), Fourier-transform infrared (FTIR), and nuclear magnetic resonance (^1H NMR) studies were used to characterize these anhydrides. The mass spectra of these compounds suggest a mechanism for their fragmentation.

*Present address: Polymeric Materials Division, Langley Research Center, NASA, Hampton, Virginia 23666.

INTRODUCTION

Phthalonitrile-capped phthalimido anhydrides derived from 4-aminophthalonitrile and various bisphthalooanhydrides are important precursors for the controlled synthesis of new phthalonitrile resins of varying flexibility and overall polarity. The phthalonitriles of varying molecular weights and linking groups are presently being evaluated as potential resins for advanced thermally stable polymers and electrically conductive polymers.

Previous studies [1-7] on phthalonitrile resins have dealt with short linking units between the phthalonitrile polymerization sites, and the results have been reported mostly through patents. Imide-containing bisphthalonitriles which are produced by reacting a bisphthalic anhydride derivative with an aromatic diamine and an aromatic compound containing two ortho cyano groups and one amino group have been reported in the patent literature [8, 9]. This method of preparation of bisphthalonitriles may involve side reactions in addition to producing nonuniform bisphthalonitrile derivatives which may adversely affect the properties of the polymeric materials produced. In order to overcome this difficulty, phthalonitrile-capped phthalimido anhydrides have been synthesized to provide better control of the synthesis reaction of homogeneous imidobisphthalonitriles, more particularly for those imidobisphthalonitriles in which terminal phthalonitriles are linked through long flexible groups.

In this paper we report the synthesis and characterization of phthalonitrile-capped phthalimidoanhydrides.

EXPERIMENTAL

Materials and Reagents

4-Aminophthalonitrile (4-APN) (Eastman Kodak Co., USA) was purified by recrystallization twice from water, mp 181-182°C. Hexafluoroisopropylidenediphthalic anhydride (6FA) (E. I. du Pont de Nemours & Co., U.S.A.), mp 240-242°C; 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA) (Koch Light, England), mp 285-286°C; 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPTDA) (Koch Light, England), mp 224-225°C; and bisesterphthalic anhydride [10], mp 274-275°C, were obtained in pure form by recrystallization from dry acetic anhydride. N,N'-dimethylacetamide (DMAC) was distilled over phosphorus pentoxide.

General Synthesis

The reactions were carried out in a three-necked flask equipped with a nitrogen inlet and outlet. The reagents were added in the sequences and stoichiometrics indicated below and in Table 1. The

TABLE 1. Preparation and Elemental Analysis of Phthalonitrile Phthalimido Anhydrides IV, V, and VI

Compound	4-Aminophthalonitrile		Bisphthalic anhydride		Yield, %	Molecular formula	Microanalysis			
	g	mol	Type	Amount g mol			Calc:	Found:	C, %	H, %
IV	1.43	0.01	PMDA	1.94	0.01	90	$C_{18}H_5N_3O_5$	62.97	1.45	12.24
								63.10	1.52	12.50
V	1.43	0.01	BPTDA	3.22	0.01	85	$C_{25}H_9N_3O_6$	67.11	2.01	9.40
								67.21	2.10	9.35
VI	1.43	0.01	BEA	4.58	0.01	80	$C_{32}H_{13}N_3O_9$	65.86	2.23	7.20
								65.20	2.40	7.21

method described is that which gave optimum yield of the title compound and is not the only method by which these compounds can be produced. As an example of the general method, the preparation of phthalonitrile-phthalimido anhydride (III) is given.

Into a continuously stirred solution of 4-aminophthalonitrile (I) (1.43 g, 0.01 mol) in DMAC (35 mL), dry nitrogen gas was bubbled. To this solution, granular hexafluoroisopropylidenediphthalic anhydride (6 FA) (4.44 g, 0.01 mol) was added. The resulting reaction mixture was allowed to stir for 1-2 h at ambient temperature to give a yellow solution of the corresponding phthalamic acid (II). The phthalamic acid solution was cyclodehydrated in situ by heating it in an aluminum dish placed in an air oven at 75°C. The residue obtained was further heated in vacuum at 165°C for 1.5 h to give phthalonitrile phthalimido anhydride (III).

Analysis. Calculated for $C_{27}H_9N_3O_5F_6$: C, 56.94; H, 1.58; N, 7.58; F, 20.05%. Found: C, 56.20; H, 1.62; N, 7.52; F, 20.12%.

By a similar method, phthalonitrile-capped phthalimido anhydrides (IV), (V), and (VI) were obtained by the reaction of 4-aminophthalonitrile with bisphthalonhydrides PMDA, BPTDA, and BEA, respectively. Their preparation, yield, and elemental analysis are given in Table 1. A portion of bisphthalonitrile was also formed.

RESULTS AND DISCUSSION

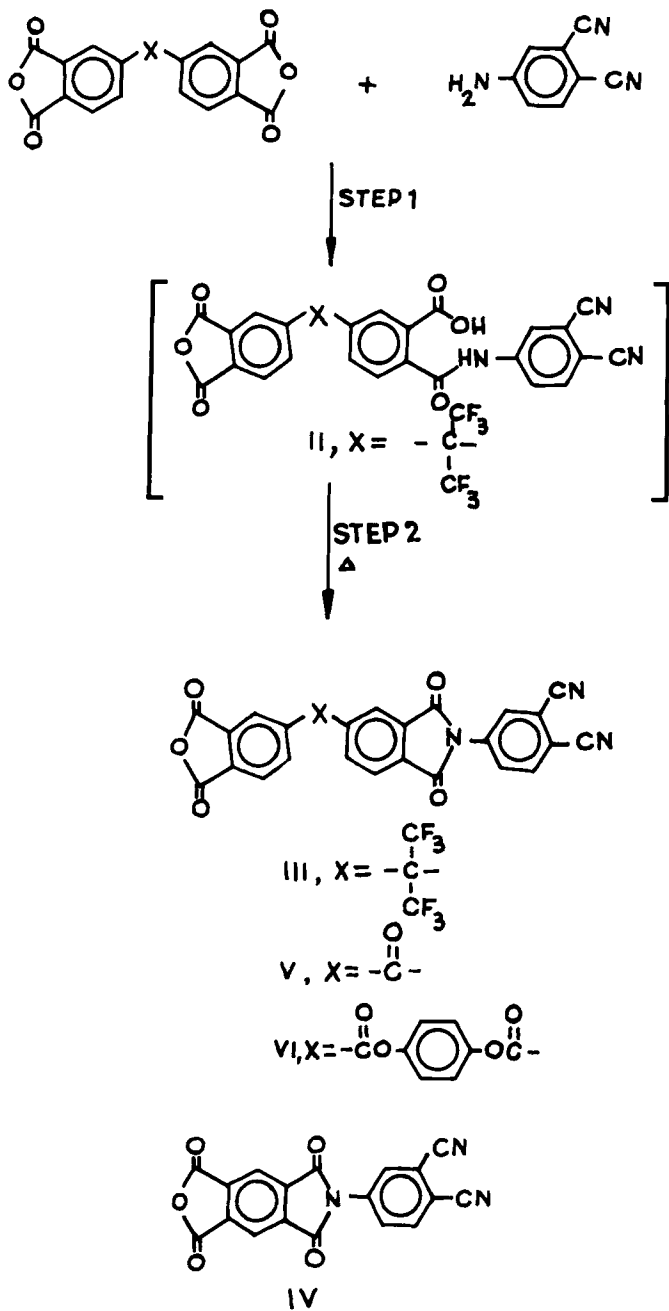
The reaction of 4-aminophthalonitrile (4-APN) with various bisphthalonhydrides, viz., 6FA, PMDA, BPTDA, and BEA, was conducted by the solution condensation technique followed by thermal cyclodehydration [11-13] to give the imide ring. The reaction sequence is given in Scheme 1.

Imide Synthesis

Condensation

The first step of solution condensation of 4-aminophthalonitrile with any of the bisphthalonhydride was performed in an aprotic solvent, N,N' -dimethylacetamide (DMAC) or N,N' -dimethylsulfoxide (DMSO). Solvents like N,N' -dimethylformamide and N -methylpyrrolidone can also be used. The addition of solid dianhydride to the amine solution was adopted [13] here to avoid premature hydrolysis of the bisanhydride. This condensation reaction was monitored by IR and 1H NMR spectrometry.

Figure 1 shows the NMR spectrum obtained soon after the addition of solid hexafluoroisopropylidenediphthalic anhydride (6FA) to the amine (4APN) solution. Direct comparison of this spectrum with the NMR spectra of its reactants 4 APN and 6FA indicated two major changes (Fig. 1). These are appearance of a new ortho coupled doublet at 8.40-8.26 ppm (two aromatic protons H_f and $H_{f'}$) and broadening



SCHEME 1.

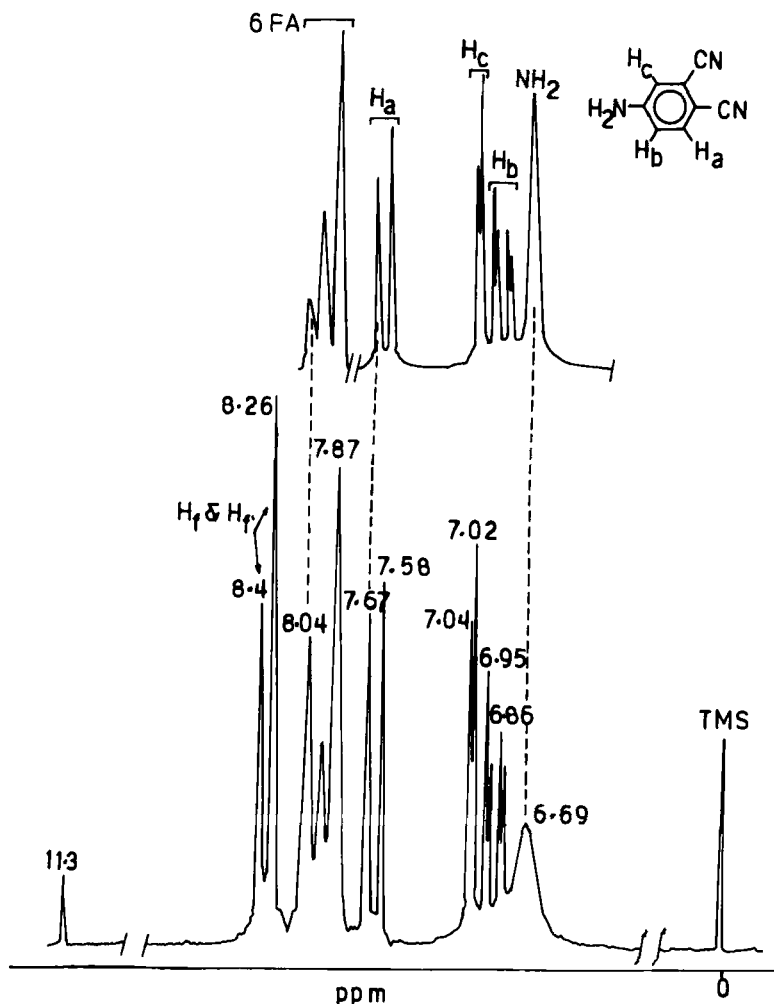
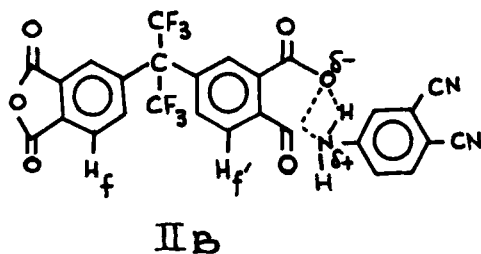
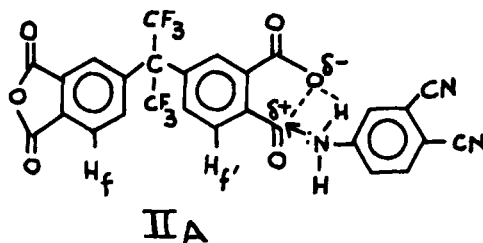


FIG. 1. ^1H NMR spectrum at 100 MHz obtained soon after addition of 6FA to 4APN solution in DMSO-d_6 .

of a D_2O exchangeable singlet at 6.69 ppm (amido-type proton). Also observed was a small exchangeable singlet at 11.30 ppm due to the presence of carboxylic proton. The downfield shift of 0.4 ppm (8.0 to 8.4 ppm) for two aromatic protons H_f and $\text{H}_{f'}$, may be interpreted here as follows: Due to solvent interactions, the molecule is oriented in such a way that, because of the diamagnetic anisotropy, these protons come in the deshielding zone of the adjacent double bonds. The

observation of the same pattern and chemical shifts of the aromatic protons from the 4APN moiety gave an indication that the chemical environment of the amino group after the reaction remains almost similar to that of parent 4APN amine. Based on this and the integrations of the observed signals, it can be said that the species may have a structure that can be represented either as II_A or II_B.



The observed identical chemical shifts of the aromatic protons H_f and H_{f'} in Structure II_A or II_B as an ortho coupled doublet indicates that this structure is not present in the free form. Perhaps fast intermolecular or intramolecular exchange aided by the solvent is responsible.

In the proton NMR spectrum of this sample recorded after about 2 h the singlet at 6.69 ppm changes to a coalescing hump, indicating the time required for this reaction giving phthalamic acid II to reach an equilibrium state. NMR monitoring of the reaction of 4APN with PMDA indicated instantaneous formation of the corresponding phthalamic acid IV.

This NMR study suggests that electrophilicity of the bisphthalon-anhydrides for reaction with 4APN lies in the order PMDA > BPTDA > 6FA > BEA.

The infrared spectrum of phthalamic acid II corresponded to its structure. The absorption bands due to the primary amino group of the amine 4APN at 3 485 and 3 381 cm⁻¹ disappeared; instead absorption at 3 500 to 3 250 cm⁻¹ due to NH arose.

Imidization

The second step of imidization was carried out by using the efficient thermal cyclodehydration reaction. Heat treatment at 165°C for almost 1 h of the residue obtained after removing solvent of phthalamic acid II at 75°C afforded the cyclodehydrated product, phthalonitrile-capped phthalimido anhydride III.

Figure 2 shows the IR spectrum of phthalimido anhydride III. The presence of characteristic strong bands at 1788 and 1721 cm^{-1} confirmed the formation of the imide ring. The strong absorption at 2237 cm^{-1} showed the presence of the phthalonitrile group. A medium and a strong band at 1936 cm^{-1} (asymmetric anhydride carbonyl) and 1855 cm^{-1} (symmetric anhydride carbonyl) showed the presence of phthalic anhydride groups. The presence of a fluorinated alkyl group was indicated by the cluster of bands at 1250 to 1120 cm^{-1} .

Figure 3 shows the NMR spectrum of phthalimido anhydride III. The observed downfield shift of the phthalonitrile aromatic protons H_b and H_c indicated the completion of the cyclodehydration reaction to give the imide III. The H_f and $H_{f'}$ protons are most deshielded and observed at 8.40-8.30 ppm.

Phthalonitrile-capped phthalimido anhydride IV, V, and VI were similarly obtained by the reaction of 4APN with pyromellitic dianhy-

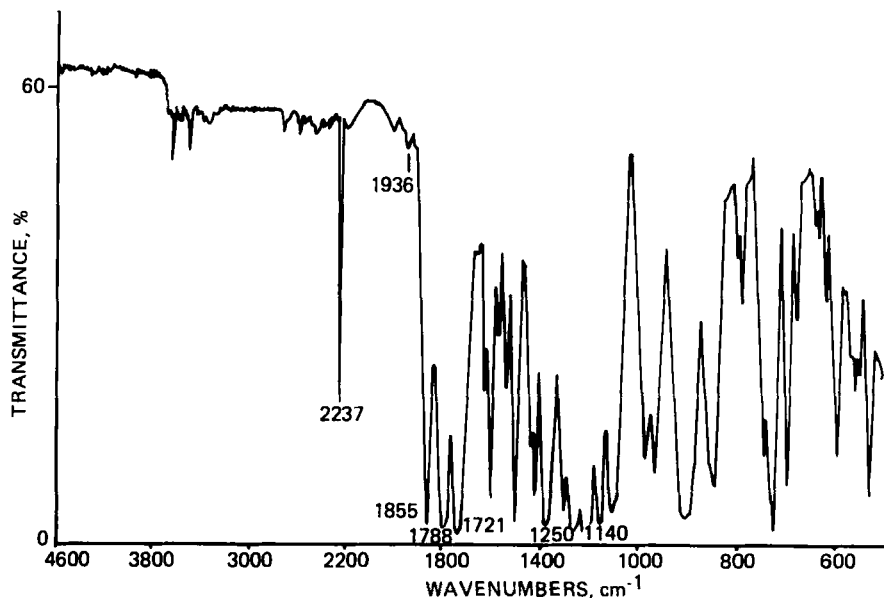


FIG. 2. Infrared spectrum of III on NaCl disk.

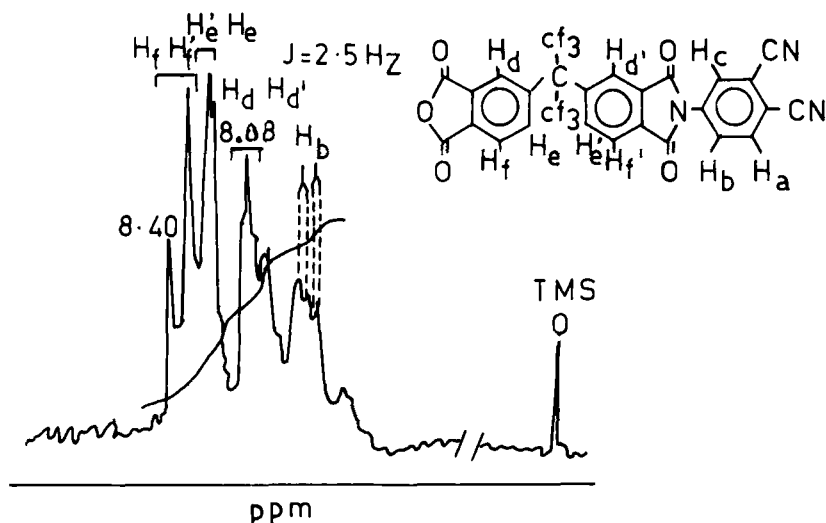


FIG. 3. ^1H NMR spectrum at 100 MHz of III in DMSO-d_6 .

dride, benzophenonetetracarboxylic dianhydride, and bisester anhydride, respectively, followed by cyclodehydration of the corresponding phthalamic acids. A small portion of bisphthalonitrile was also formed.

Figure 4 shows the IR spectrum of phthalimido anhydride IV. It shows the presence of imide (1778 and 1726 cm^{-1}), phthalic anhydride (1936 and 1853 cm^{-1}), and phthalonitrile (2236 cm^{-1}) groups. Infrared spectra of phthalimido anhydrides V and VI were similarly in agreement with their structures.

Figure 5 shows the NMR spectrum of phthalimido anhydride IV. The downfield shift of phthalonitrile aromatic protons, together with their parent pattern of splitting, indicated formation of the imide group. The doublet at 8.40 – 8.32 ppm was due to ortho-coupled H_a proton. A doublet of doublets due to H_b proton was observed at 8.13 and 8.05 ppm. The H_d and H_d' protons of PMDA were seen at 8.62 ppm. All the signals showed the appropriate integrated areas.

Figure 6 shows the NMR spectrum of phthalimido anhydride V. The observed downfield shift was of the same order as observed for the similar compounds III and IV, indicating formation of the imide ring. The doublet of doublets for H_b aromatic protons was clearly seen at 8.13 – 8.04 ppm. The signals of the H_a and H_b aromatic protons were seen merged with the large multiplet for benzophenone aromatic protons.

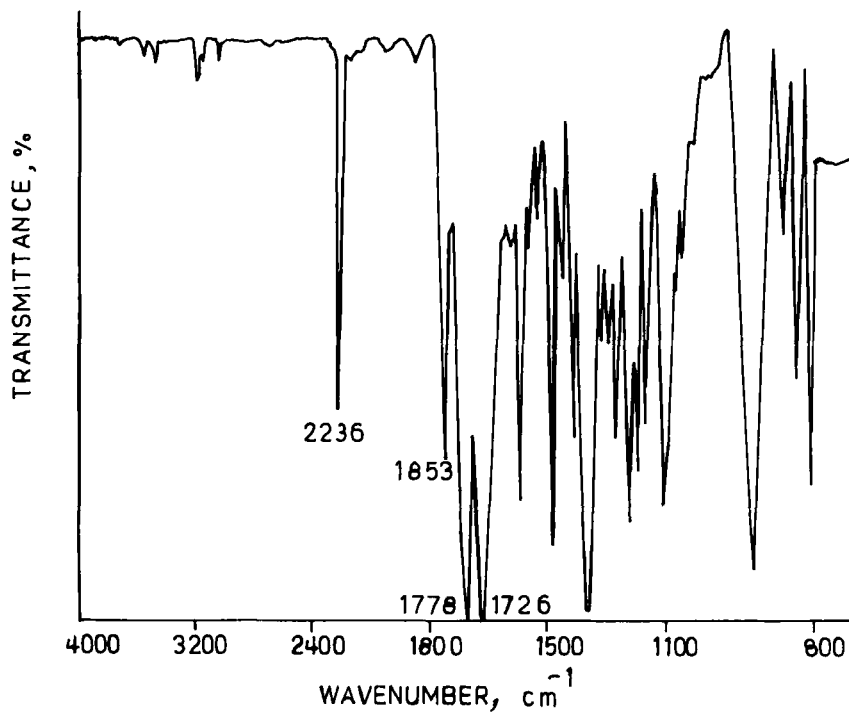


FIG. 4. Infrared spectrum of IV on NaCl disk.

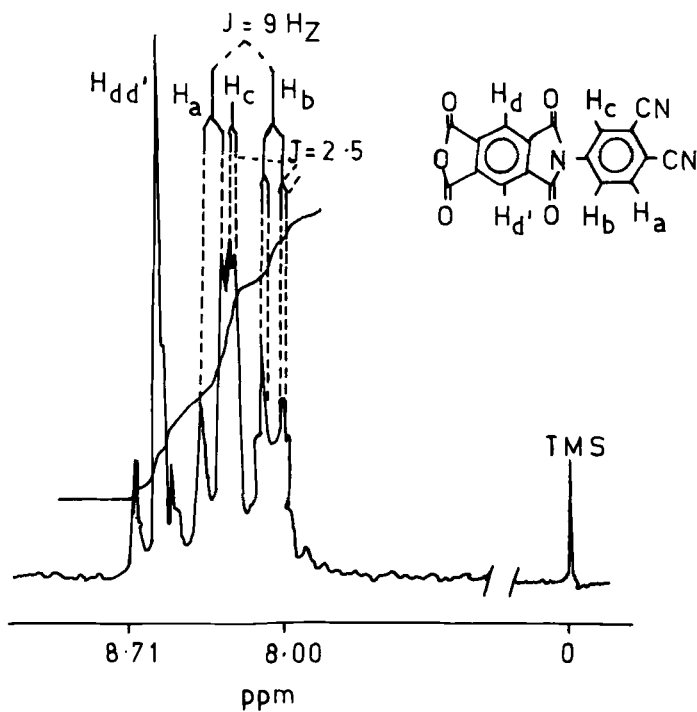


FIG. 5. ^1H NMR spectrum of IV in DMSO-d_6 .

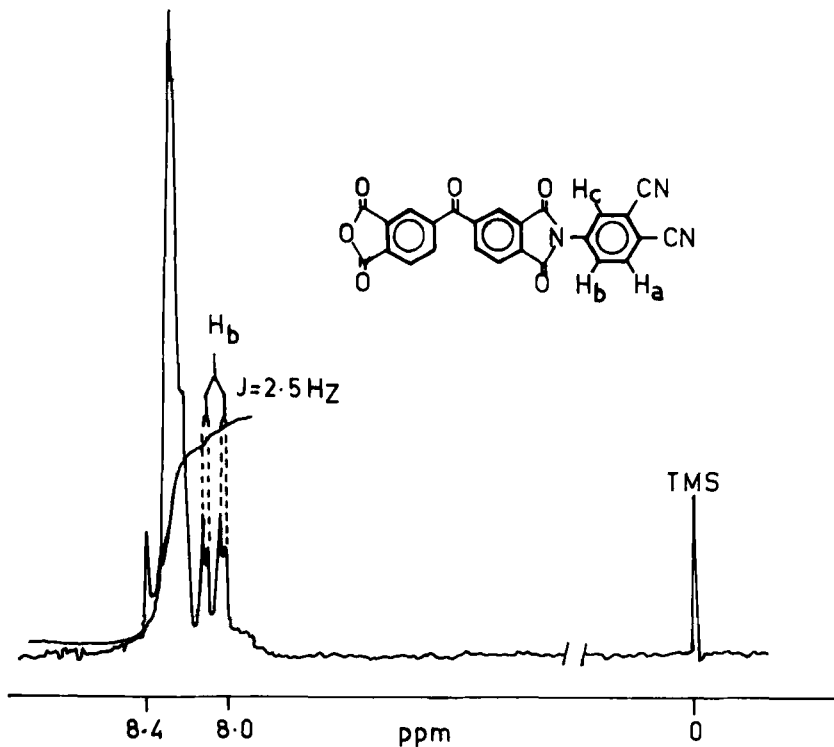


FIG. 6. ^1H NMR spectrum of V in DMSO-d_6 .

DSC Analysis

The DSC studies of the synthesized phthalimido anhydrides are presented in Fig. 7, which shows a sharp endotherm at 296°C , indicating melting of phthalimido anhydride IV.

Mass Spectra

The mass spectra of phthalonitrile-capped phthalimido anhydride III and IV are presented in Figs. 8 and 9, respectively. The positively charged fragments with their relative intensities are summarized in Table 2.

The base peak for Compound III was observed at mass ion m/e 400. Observation of the parent ion ($\text{C}_{27}\text{H}_9\text{N}_3\text{O}_5\text{F}_6^+$) at m/e 569 substantiated the Structure III to this compound. The $(M + 1)^+$ ion peak at m/e 570, with its relative abundance 4.2, agrees well with the calculated value. In Compound IV the parent ion peak ($\text{C}_{18}\text{H}_5\text{N}_3\text{O}_5^+$) at m/e 343

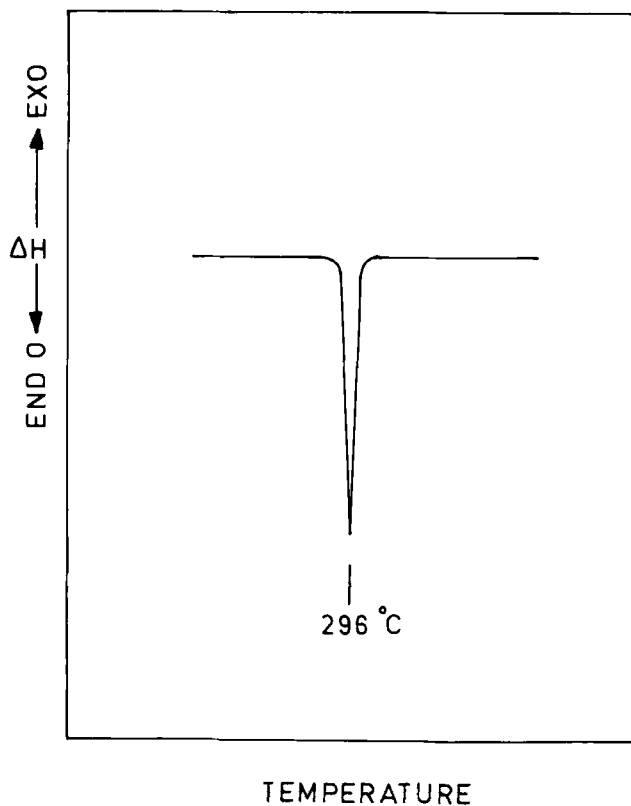


FIG. 7. DSC curve of IV in nitrogen. Heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, $100\text{ mL}/\text{min}$.

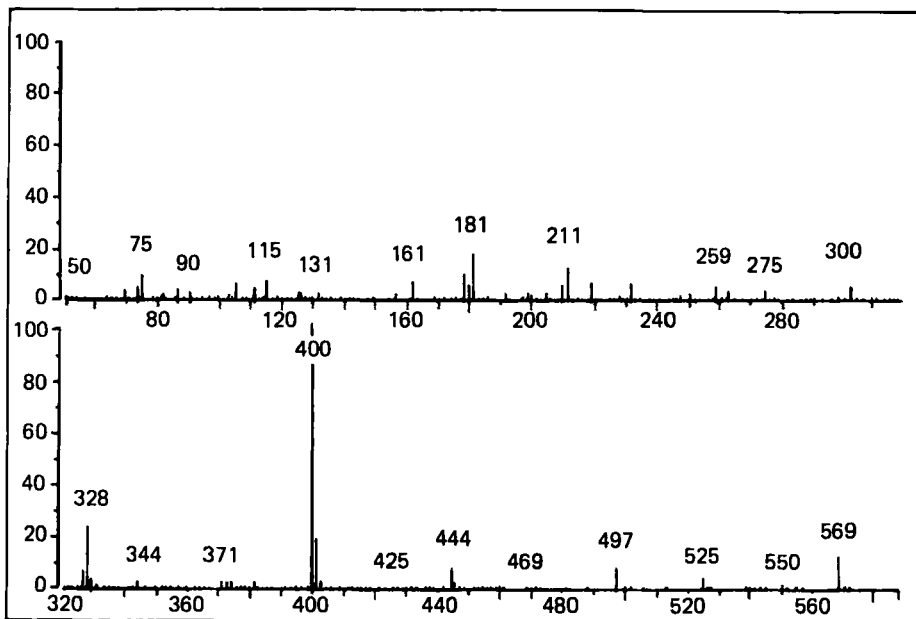


FIG. 8. Mass spectrum of III.

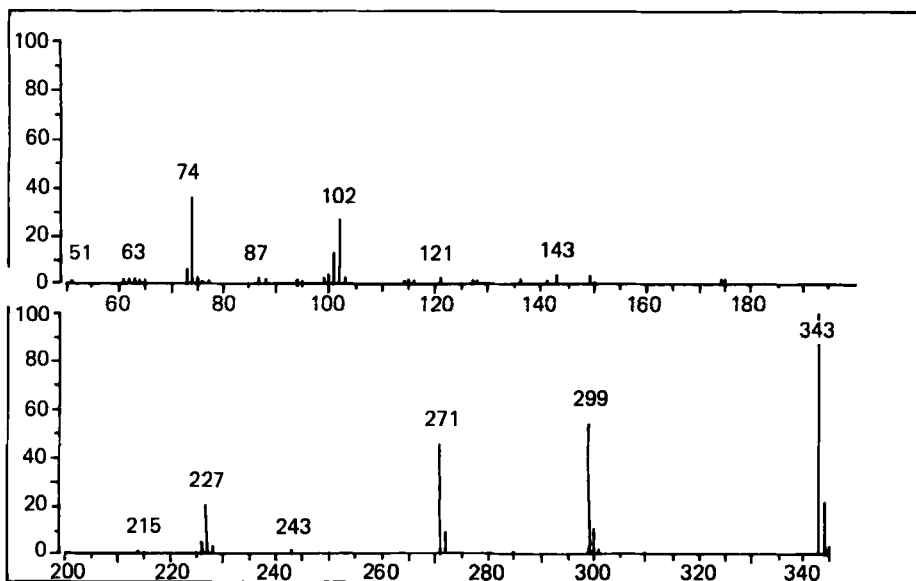


FIG. 9. Mass spectrum of IV.

TABLE 2. Major Ion Fragments and Relative Intensities of Phthalonitrile-Capped Phthalimido Anhydrides III and IV

Number	Compound III		Compound IV	
	m/e	Relative intensity	m/e	Relative intensity
1	74	5.5	73	6.6
2	75	10.7	74	36.1
3	115	8.7	75	3.7
4	161	7.7	100	4.0
5	178	11.1	101	12.8
6	180	6.3	102	27.2
7	181	18.7	103	2.2
8	210	6.2	121	2.6
9	211	13.7	143	4.1
10	259	5.5	226	5.3
11	300	8.1	227	20.3
12	327	7.4	271	45.4
13	328	23.9	272	9.1
14	400	100.0 (base peak)	299	54.5
15	401	19.9	300	10.5
16	444	8.5	343	100.0 (base and parent peak)
17	497	7.9	344	21.9
18	525	3.9	345	3.5
19	569	13.3 (parent peak)		
20	570	4.2		

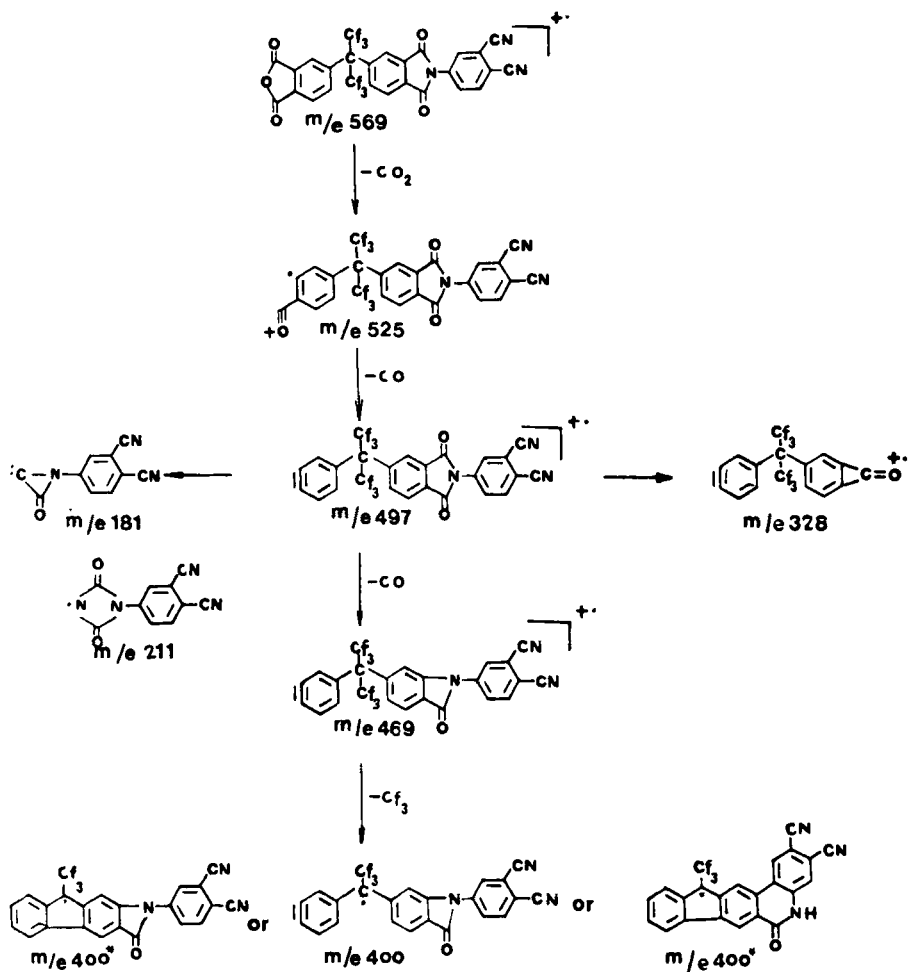


FIG. 10. Mass spectral fragmentations for Compound III. The structure shown for m/e 400* may arise by possible rearrangement reactions.

is the base peak, indicating its greater stability over Compound III. The relative intensity of the $(M + 1)^+$ peak is 21, substantiating the Structure IV. It can be seen from the pattern of fragmentations shown for Compounds III and IV (Figs. 10 and 11) that, for these compounds, CO_2 and CO loss is a preferential mode of fragmentation arising initially from the phthalic anhydride ring present.

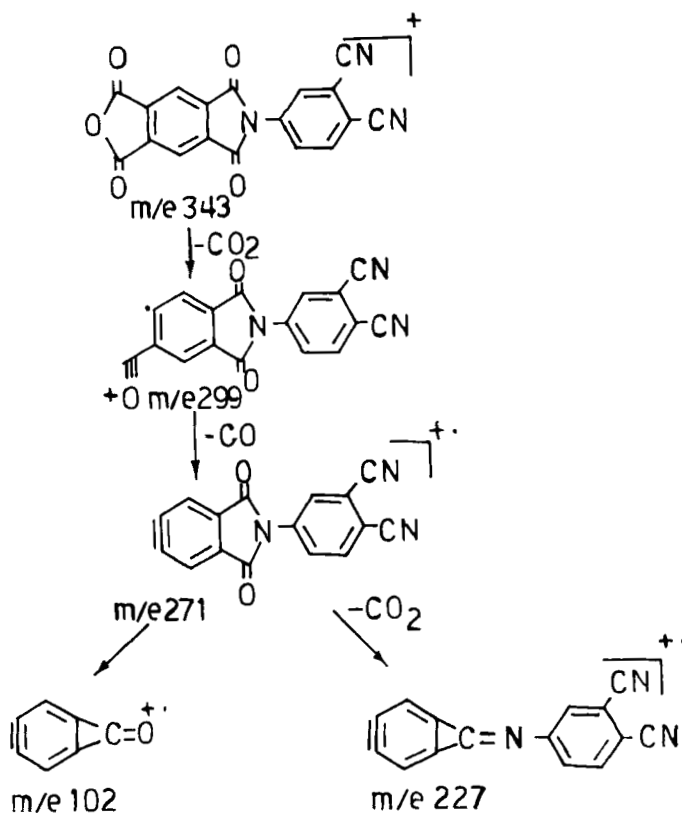


FIG. 11. Mass spectral fragmentations for Compound IV.

REFERENCES

- [1] J. R. Griffith and J. G. O' Rear, U.S. Patent 3,993,631 (1976).
- [2] J. R. Griffith and J. G. O' Rear, U.S. Patent 4,067,860 (1978).
- [3] T. M. Keller and J. R. Griffith, U.S. Patent 4,234,712 (1980).
- [4] J. R. Griffith and T. M. Keller, U.S. Patent 4,238,601 (1979).
- [5] T. M. Keller, T. R. Price, and J. R. Griffith, *Synthesis*, p. 613 (1980).
- [6] T. M. Keller, T. R. Price, and J. R. Griffith, *J. Org. Coat. Plast. Prep.*, **43**, 804 (1980).
- [7] T. M. Keller and J. R. Griffith, "Resins for Aerospace," *Am. Chem. Soc., Symp. Ser.*, **25**, 132 (1980).
- [8] G. F. D'Alelio, U.S. Patent 3,890,274 (1975).

- [9] G. F. D'Alelio, U.S. Patent 3,996,196 (1976).
- [10] D. F. Loncrini, J. Polym. Sci., Part A-1, 4, 1531 (1966), p-phenylenebis(trimellitate)dianhydride produced from trimellitic anhydride and p-phenylene diacetate.
- [11] C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Oliver, J. Polym. Sci., Part A, 3, 1373 (1965).
- [12] D. Kumar, J. Polym. Sci., Polym. Chem. Ed., 18, 1375 (1980).
- [13] D. Kumar, Ibid., 19, 795 (1981).

Received August 9, 1985