

Journal of Molecular Structure 448 (1998) 1-9

# Isobenzofuran (IBF) precursor characterization using IR, NMR, X-ray and thermogravimetric analysis

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Received 30 October 1997; revised 14 January 1998; accepted 14 January 1998

#### Abstract

The Diels-Alder (DA) addition product of epoxynaphthalene with tetraphenylcyclopentadienone serves as a precursor for isobenzofuran (IBF), one of the most reactive dienes known.

A detailed investigation on the DA reaction of epoxynaphthalene with tetraphenylcyclopentadienone shows, that in addition to the main, commonly described DA product [Fieser and Haddadin, J. Am. Chem Soc. 86 (1964) 2081; Fieser and Haddadin, Can. J. Chem. 43 (1965) 1599], another stereoisomer by-product is formed. The two isomers are compared with respect to their thermal and spectroscopic properties. Spectroscopic investigations show that Fieser's assumed exo,exo-configuration for the main product is indead an exo,endo-configuration. The by-product turns out to be the exo,exo-stereoisomer. © 1998 Elsevier Science B.V. All rights reserved

Keywords: Characterization; Isobenzofuran; Cyclopentadienone; Stereoisomer

#### 1. Introduction

It is often reported in the literature that Diels-Alder (DA) reactions lead to a single stereoisomer [1-5]. However, the formation of several isomers is theoretically possible. Stereochemical different DAadducts, e.g. an exo- versus endo-product, usually exhibit different physico-chemical properties [3-5]. The determination of the stereochemistry of the products formed is important in the determination of property-structure relationships. Isobenzofuran (IBF) **1** is one of the most reactive dienes known [6-9]. This is because in a DA reaction IBF generates an energetically favored benzene moiety (Scheme 1). IBF is easily generated by thermal decomposition of the precursor 4 through a pericyclic decarbonylation of 4 followed by retro-DA reaction of the decarbonylation product 5 (Scheme 2).

In general, it is favorable to perform a DA reaction at the lowest possible temperature, because the higher the temperature, the greater the likelihood of a retro-DA reaction. In that respect, a lower IBF formation temperature makes a retro-DA reaction less likely. Therefore, dienophiles that are thermally unstable would be accessible to react with IBF.

The DA-reaction of epoxynaphthalene 7 with cyclopentadienone 8 (Scheme 3) has first been described in Refs [1,2]. The yield of DA-adduct 4 was reported to be quantitative in one case [1] and almost quantitative [2] (97.6% isolated) in another.

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Scheme 1. Aromatization of the IBF moiety as the driving force of IBF's diene reactivity.

No indication of another stereoisomer was published. The adduct was described by the authors as the exo,exo-adduct **4b** (Fig. 1).

Whereas the exo-attack of the diene could be proved by the lack of coupling of the vicinal protons H9,10 and H4a,9a (Fig. 1), the exo-orientation of the carbonyl bridge was based solely on the relatively high melting point [mp: 180–184°C (dec.) [1,2]]. The exo,exo-configuration) was questioned by Kanematsu and co-workers [12] based on NMR coupling experiments [13] of DA-adducts of epoxide 7 with other cyclopentadienones. Also, Mackenzie et al. [11] assumed an exo,endo-product rather than the exo,exo-product.

To the best knowledge of the authors, a proof of the absolute stereochemistry of the precursor type 4 has not been given in the literature so far [1,2,10-17].



Fig. 1. Exo,endo- (4a) and exo,exo- (4b) IBF precursor.

Consequently, the synthesis of the IBF precursor 4, through the DA reaction of epoxynaphthalene 7 and tetraphenylcyclopentadienone 8, was investigated in more depth.

## 2. Experimental

## 2.1. General considerations

All experiments were carried out under nitrogen. The chemicals used were purchased from Aldrich (tetraphenylcyclopentadienone and ethanol) and Fluka (epoxynaphthalene), and were used without further purification.



Scheme 2. Formation of IBF 1 through thermal treatment of precursor 4.



Scheme 3. Formation of IBF precursor 4.

## 2.2. Instrumental analyses

All spectra were recorded at ambient temperature. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in deuterated chloroform on a Brüker AC 300 spectrometer. Peak positions are reported in ppm and coupling constants in Hz. Signal multiplicity as well as number of protons are given in parentheses. The assignments of the signals were made on the basis of selective decoupling [13] and DEPT (distortionless enhancement by polarization transfer) experiments. FT-IR spectra were recorded using Harrick's Split Pea accessory (single reflection attenuated total reflectance [ATR]) on BIO-RAD FTS 175. Bands are reported in cm<sup>-1</sup>. Elementary analysis was done with an Elemental-Analyzer (Perkin-Elmer EA 240), as well as Heraeus CHN-Rapid. The thermogravimetric analysis was done under nitrogen at a rate of 5 K/min with a Mettler TG 50. The melting point was determined with a Reichert Thermovar melting point microscope. The reported values are not corrected. Electron impact mass spectra were recorded with Finnigan-MAT CH 7A (EI 70 eV). The relative intensity of the peak is given in parentheses in per cent, followed by its assignment. UV spectra were recorded using a Perkin-Elmer Lambda 3 spectrometer. The solvents used are given in parentheses. The values represent  $\lambda_{max}$  with log e given in parentheses.

## 2.3. X-ray structure determination of 4a and 4b

Enraf-Nonius CAD-4 diffractometer, at ambient temperature using  $Cu_{K\alpha}$  radiation ( $\lambda = 1.5418$  Å), graphite monochromator. The structures were solved by direct methods (MULTAN), empirical absorption correction, anisotropic temperature factors for O and

C, refinement of the H atoms in the 'riding mode' with fixed isotropic temperature factors.

 $(1\alpha, 4\alpha, 4a\alpha, 9\beta, 9a\alpha, 10\beta)$ -1,4,4a,9,9a,10-Hexahydro-1,2,3,4-tetraphenyl-9, 10-epoxy-1, 4-metha-(4a)and noanthracen-12-one  $(1\alpha, 4\alpha, 4\alpha\beta, 9\alpha,$  $9a\beta$ ,  $10\alpha$ )-1, 4, 4a, 9, 9a, 10-Hexahydro-1, 2, 3, 4-tetraphenyl-9,10-epoxy-1,4-methanoanthracen-12-one (**4b**) were prepared by mixing 1,4-dihydro-1,4-epoxynaphthalene (7, 14.42 g) and tetraphenylcyclopentadienone (8, 38.45 g) in ethanol (500 ml) and heated for three days under reflux and nitrogen atmosphere. The resulting precipitate is filtered and washed with ethanol (11) until it is free of tetraphenylcyclopentadienone [yield: 48.86 g (92.4%) (4a)]. Out of the ethanol filtrate, colorless crystals of 4b formed upon standing at ambient temperature over the weekend. Yield of 4b: 3.12 g (5.9%). The separation of 4a and 4b can be done by means of column chromatography over silica with toluene  $[R_f (4a) = 0.64; R_f$ (4b) = 0.41] and subsequent recrystallization from ethanol. Data for 4a are given elsewhere [1,2,8]. Compound **4b**: <sup>1</sup>H-NMR: δ 7.61–7.58 (m, 4H); 7.37–7.31 (m, 6H); 7.26–7.21 (m, 4H); 6.96–6.84 (m, 6H); 6.62-6.59 (m, 4H); 5.43 (s, 2H); 3.14 (s, 2H);  $^{13}C{^{1}H}-NMR: \delta 198.83$  (q); 145.50 (q); 144.68 (q); 134.68 (q); 130.01 (CH); 129.47 (CH); 128.19 (CH); 127.39 (CH); 127.15 (CH); 126.99 (CH); 126.88 (CH); 119.60 (CH); 1.09 (CH); 62.86 (q); 58.47 (CH); <sup>13</sup>C-NMR:  $\delta$  198.83 (t, <sup>3</sup> $J_{C,H}$  = 6.6 Hz). IR: 3078(w), 3063(w), 3051(w), 3028(m), 3018(w), 2962(w), 2950(w), 2919(w), 1948(vw), 1773(vs), 1603(w), 1578(vw), 1496(m), 1488(w), 1460(w), 1447(m), 1347(vw), 1230(vw), 1201(w), 1188(vw), 1159(w), 1113(vw), 1083(vw), 1073(vw), 1027(vw), 1010(vw), 1001(vw), 994(w), 988(w), 952(m), 943(w), 923(w), 861(vw), 852(m), 841(w), 835(w), 829(m), 794(w), 777(w), 759(s), 736(m), 728(w), 698(vs), 678(w), 654(m), 640(w), 621(vw), 610(vw), 573(w), 554(w), 531(m). UV (CH<sub>2</sub>Cl<sub>2</sub>): 258 (3.874); 263.5 (3.866); 270 (3.830); (cyclohexane): 224 (2.919); 258.5 (2.455); 265 (2.481); 271.5 (2.463); 285 sh (2.279). MS: m/z (relative intensity) 529 (2.35; M<sup>+</sup> + 1); 528.1 (5.12; M<sup>+</sup>); 382.2 (70.19; 3'6'-diphenyl-1,1':2',1"-terphenyl); 118.1 (100; isobenzofuran). TGA: 246.3°C (dec.), mp.: 241.3°C (dec.). Anal. Calcd. for  $C_{39}H_{28}O_2$  (528.66): C, 88.61; H, 5.34. Found: C, 88.68; H, 5.41.

#### 3. Results

## 3.1. Unexpected finding

When the DA reaction of epoxide 7 and cyclopentadienone 8 is done in boiling ethanol, another previously not described by-product crystallizes from the ethanol filtrate [18]. A detailed investigation by means of NMR, X-ray, IR and thermogravimetric analysis on both products was therefore carried out.

#### 3.2. Infrared analysis

The infrared (IR) spectra of both crystalline materials are very similar, showing, in general, only minor band shifts. In both cases, the peaks with the highest intensity are at  $1775 \text{ cm}^{-1}$  and 698 cm<sup>-1</sup>. The by-product shows two bands that can not be found in the main product at 2951 cm<sup>-1</sup> and 2964 cm<sup>-1</sup>. In the fingerprint region, peaks at  $509 \text{ cm}^{-1}$  and  $980 \text{ cm}^{-1}$  seem to be characteristic for the main product, whereas this is the case at  $530 \text{ cm}^{-1}$ and 953 cm<sup>-1</sup> for the by-product (Fig. 2). A comparison of both products in the fingerprint region, especially between  $600 \text{ cm}^{-1}$  and  $900 \text{ cm}^{-1}$ . shows a 'flip-flop'-like pattern of signal intensities: bands with a high intensity in one product have a low intensity in the other product, and vice versa.



Fig. 2. Fingerprint region of 4a (dotted line) and 4b (connected line).



Fig. 3. Coupled <sup>13</sup>C-NMR of main product 4a and by-product 4b.

## 3.3. NMR analysis

The NMR spectrum of the main product [11] and that of the by-product, shown in the experimental section, differ, yet both have features that would be expected for a DA adduct of epoxide 7 and cyclopentadienone 8. In both cases the <sup>1</sup>H-NMR shows the expected ratio of aromatic to epoxy-bridge (H5 and H9) to the carbon-bridge protons (H4a and H10a). The four bridge protons appear as singlets. In the <sup>13</sup>C{<sup>1</sup>H}-NMR, the situation is similar: both spectra show the expected signals for the aromatic, carbonyl, epoxy (C9 and C10), as well as the bridge (C4a and C9a) carbons in the expected region. A



Fig. 4. ORTEP drawing of main product 4a and by-product 4b.

coupling experiment described elsewhere [12] revealed no coupling for the carbonyl carbon of the main product, but a coupling of 6.6 Hz for the by-product (Fig. 3).

# 3.4. X-ray analysis

Well formed white crystals of both reaction products were therefore obtained by recrystallization and analyzed. Crystals precipitated from ethanol had a hexagonal morphology for the main product and a rhombic morphology for the by-product. The crystals of the by-product where about 10 times larger than those for the main product. X-ray analysis shows the absolute configuration of the two products **4a** and **4b** (Fig. 4).



Fig. 5. Thermogravimetric analysis (TGA) of 4a (A) and 4b (B).

Table 1 Positional parameters and their estimated standard deviations of 4a in Å

Name	x	Y	Z	B <sub>equ</sub>
01	0.4521(1)	0.09464(8)	0.1434(1)	4.50(4)
O2	0.2487(1)	-0.15104(8)	0.0869(1)	4.06(4)
Cl	0.4041(2)	0.0384(1)	0.1424(2)	3.31(5)
C2	0.4436(2)	-0.0428(1)	0.1600(2)	3.10(5)
C3	0.3981(2)	-0.0590(1)	0.2549(2)	3.09(5)
C4	0.3062(2)	-0.0203(1)	0.2338(2)	3.19(5)
C5	0.2852(2)	0.0246(1)	0.1248(2)	3.22(5)
C6	0.2614(2)	-0.0305(1)	0.0241(2)	3.19(5)
C7	0.3670(2)	-0.0730(1)	0.0440(2)	3.15(5)
C8	0.3274(2)	-0.1540(1)	0.0329(2)	3.80(6)
C9	0.1829(2)	-0.0953(1)	0.0140(2)	3.77(5)
C10	0.2590(2)	-0.1654(1)	-0.0891(2)	3.98(6)
C11	0.1641(2)	-0.1287(1)	-0.0999(2)	3.89(6)
C12	0.0826(2)	-0.1255(2)	-0.2015(2)	5.20(7)
C13	0.0971(2)	-0.1605(2)	-0.2923(2)	6.36(8)
C14	0.1898(3)	-0.1961(2)	-0.2831(2)	6.51(8)
C15	0.2734(2)	-0.1986(2)	-0.1807(2)	5.48(7)
C16	0.5607(2)	-0.0540(1)	0.1858(2)	3.21(5)
C17	0.6338(2)	-0.0137(2)	0.2709(2)	4.52(6)
C18	0.7417(2)	-0.0238(2)	0.2954(2)	5.46(7)
C19	0.7782(2)	-0.0753(2)	0.2364(2)	5.22(7)
C20	0.7076(2)	-0.1153(1)	0.1523(2)	4.46(6)
C21	0.5995(2)	-0.1045(1)	0.1263(2)	3.70(5)
C22	0.4498(2)	-0.1086(1)	0.3510(2)	3.10(5)
C23	0.5049(2)	-0.1717(1)	0.3398(2)	3.68(5)
C24	0.5542(2)	-0.2167(1)	0.4322(2)	4.41(6)
C25	0.5491(2)	-0.1996(1)	0.5362(2)	4.55(6)
C26	0.4946(2)	-0.1376(1)	0.5486(2)	4.62(6)
C27	0.4462(2)	-0.0925(1)	0.4581(2)	3.89(6)
C28	0.2287(2)	-0.0293(1)	0.2927(2)	4.02(6)
C29	0.1850(2)	-0.0989(2)	0.2955(2)	5.59(7)
C30	0.1143(2)	-0.1099(2)	0.3517(2)	8.1(1)
C31	0.0849(2)	-0.0524(3)	0.4048(3)	8.8(1)
C32	0.1263(2)	0.0163(2)	0.4033(2)	8.49(9)
C33	0.1981(2)	0.0285(2)	0.3475(2)	6.38(7)
C34	0.2166(2)	0.0931(1)	0.1048(2)	3.61(5)
C35	0.2509(2)	0.1540(1)	0.1743(2)	5.35(7)
C36	0.1951(2)	0.2196(2)	0.1542(3)	6.73(9)
C37	0.1037(2)	0.2258(2)	0.0643(3)	6.15(8)
C38	0.0670(2)	0.1665(1)	-0.0063(2)	5.04(7)
C39	0.1232(2)	0.1007(1)	0.0144(2)	4.01(6)

Positional parameters and their estimated standard deviations for both isomers are given in Tables 1 and 2. A comparison of the crystallographic important data of **4a** and **4b** is given in Table 3.

# 3.5. Thermal analysis

A thermogravimetric analysis of the two isomers

reveals the same pattern for both isomers, yet the exo,exo-product **4b** has an  $\approx 60^{\circ}$ C higher decomposition temperature than the exo,endoproduct **4a** (Fig. 5). When both products were heated up to the end of the first major weight loss step, only tetraphenylbenzene **6** is identified in the residue. Neither IBF precursor **4a** nor **4b** is detected.

Table 2 Positional parameters and their estimated standard deviations of 4b in Å

Name	X	Y	Z	B <sub>equ</sub>
01	0.0633(2)	0.2019(1)	0.6612(2)	4.29(5)
02	0.2799(2)	0.22060(9)	0.8574(2)	3.76(5)
C1	0.0916(3)	0.1621(1)	0.7253(3)	3.30(7)
C2	0.1924(3)	0.1093(1)	0.7285(2)	3.20(7)
C3	0.0934(3)	0.0576(1)	0.7340(2)	3.20(7)
C4	0.0005(3)	0.0777(1)	0.7911(2)	3.20(7)
C5	0.0299(3)	0.1443(1)	0.8263(2)	3.01(7)
C6	0.1533(3)	0.1416(1)	0.9109(2)	3.04(7)
C7	0.2602(3)	0.1162(1)	0.8464(2)	3.07(7)
C8	0.3614(3)	0.1672(1)	0.8623(3)	3.57(7)
C9	0.2110(3)	0.2046(1)	0.9461(3)	3.52(7)
C10	0.4174(3)	0.1660(1)	0.9792(3)	3.71(7)
C11	0.3208(3)	0.1910(1)	1.0334(3)	3.62(7)
C12	0.3350(3)	0.1956(2)	1.1436(3)	4.44(8)
C13	0.4500(3)	0.1745(2)	1.1988(3)	5.23(9)
C14	0.5457(3)	0.1489(2)	1.1463(3)	5.01(9)
C15	0.5308(3)	0.1438(2)	1.0353(3)	4.36(8)
C16	0.2816(3)	0.1065(1)	0.6430(3)	3.63(7)
C17	0.2477(4)	0.1322(2)	0.5427(3)	5.18(9)
C18	0.3295(4)	0.1296(2)	0.4647(3)	6.9(1)
C19	0.4485(4)	0.1015(2)	0.4859(3)	6.6(1)
C20	0.4827(4)	0.0748(2)	0.5840(3)	6.5(1)
C21	0.4003(3)	0.0776(2)	0.6618(3)	5.41(9)
C22	0.1073(3)	-0.0054(1)	0.6956(3)	3.69(7)
C23	0.0900(3)	-0.0538(2)	0.7637(3)	4.97(9)
C24	0.0927(4)	-0.1134(2)	0.7279(4)	6.6(1)
C25	0.1141(4)	-0.1253(2)	0.6247(4)	7.3(1)
C26	0.1349(4)	-0.0785(2)	0.5574(4)	7.3(1)
C27	0.1315(4)	-0.0184(2)	0.5917(3)	5.22(9)
C28	-0.1127(3)	0.0447(1)	0.8223(3)	3.31(7)
C29	-0.1928(3)	0.0100(2)	0.7475(3)	4.53(8)
C30	-0.2981(4)	-0.0206(2)	0.7792(3)	5.8(1)
C31	-0.3253(4)	-0.0171(2)	0.8823(3)	5.8(1)
C32	-0.2476(3)	0.0170(2)	0.9573(3)	4.99(9)
C33	-0.1428(3)	0.0475(1)	0.9269(3)	3.80(7)
C34	-0.0849(3)	0.1806(1)	0.8524(3)	3.25(7)
C35	-0.1868(3)	0.1905(1)	0.7706(3)	4.19(8)
C36	-0.2979(3)	0.2202(2)	0.7912(3)	5.01(9)
C37	-0.3093(3)	0.2400(2)	0.8931(3)	5.34(9)
C38	-0.2104(3)	0.2299(2)	0.9758(3)	4.74(9)
C39	-0.0990(3)	0.2003(1)	0.9547(3)	3.79(7)

# 4. Discussion

IR and NMR spectra of both products correlate with a DA adduct of epoxide 7 and cyclopentadienone 8.

The highest intensity bands in the IR, at  $1175 \text{ cm}^{-1}$  and 698 cm<sup>-1</sup>, are assigned to the carbonyl bridges and the H-C (aromatic) out-of-plane bending, respectively. The pattern in the signal intensities of the two

isomers, seen in the fingerprint region, is noteworthy. The relative intensities of some bands are reversed. The presence of bands at  $2951 \text{ cm}^{-1}$  and  $2964 \text{ cm}^{-1}$  seems to establish the existence of the by-product by IR. The bands at  $980 \text{ cm}^{-1}$  and  $509 \text{ cm}^{-1}$  for the main product, and  $953 \text{ cm}^{-1}$  and  $530 \text{ cm}^{-1}$  for the by-product should distinguish between the two products, even when a mixture of both is present.

Table 3 Comparison of crystallographic data of **4a** and **4b** 

	4a	4b
a[Å]	13.3805(9)	10.4126(5)
<i>b</i> [Å]	18.0099(14)	21.9299(20)
<i>c</i> [Å]	12.6119(6)	12.5595(39
α[°]	90	90
β[°]	110.040(3)	97.075
γ[°]	90	90
V[Å <sup>3</sup> ]	2855.2	2846.1
Z	4	4
$D_{\rm X}[\rm g cm^{-3}]$	1.22	1.234
Space group	$P2_1/c$	$P2_1/c$
Number of reflections measured	3732	3767
Number of 'observed' reflections $[I > 3s(I)]$	2998	2656
R	0.041	0.037
Rw	0.066	0.038
μ	5.44	5.46

The lack of  ${}^{3}J_{H,H}$  coupling [19] in the NMR for the bridge protons indicates that the epoxide 7 is approached by the diene 8 at its exo-face. Both spectra show that the dienophile added the diene at its exo-face. Only the  ${}^{3}J_{C,H}$  coupling of the carbonyl carbon revealed the orientation of the carbonyl bridge with respect to the epoxy bridge. The lack of coupling in the main product **4a** indicates the formation of an exo,endo-product, whereas the coupling in the by-product indicates an exo,exo product **4b**.

Indeed, the X-ray analysis confirmed the assignment based on NMR experiments. NMR and X-ray analysis both proved that the original assignment [1,2] of the stereochemistry of the main DA-adduct of epoxide 7 with cyclopentadienone 8 was incorrect. The stereochemistry assumed by Kanematsu and coworkers [12] could be proven for the first time. Both products are a DA adduct resulting by adding the diene 8 at the exo-face of the dieneophile 7. No adduct formed by adding the diene at the endo-face of epoxide 7 was detected. Since more than 98% of the theoretically possible product could be isolated and identified, at most only small amounts of endo.endoor endo, exo-DA adduct may form. The thermogravimetric analysis shows that the two products differ significantly in their properties. Their difference in thermal behavior is significant because the adducts serve as precursors for isobenzofuran (IBF). The exo, exo-product is thermally more stable than the exo,endo-product. This correlates with the findings of similar DA adducts of epoxide 7 where the exo,endo-isomer is also less stable than the exo,exoisomer [11]. The steps seen in the thermogravimetric analysis pattern are mainly assigned to the loss of carbon monoxide and IBF ( $\approx 25\%$  weight loss), as well as tetraphenylbenzene ( $\approx$ 72%). The weight loss above 300°C is attributed to the decomposition of a formed polymeric material [18]. At higher temperature (compare decomposition of 4b with 4a) 4b forms more of a polymeric residue than 4a.



4a



A lower degradation temperature for IBF precursor 4 allows for studies using dieneophiles that are more sensitive to thermal decomposition. The isomer with the highest decomposition temperature is of interest with adducts that are formed at elevated temperatures. Since DA reactions are preferably run at lower reaction temperatures, the main product, 4a, is of more interest as an IBF precursor than 4b. As was demonstrated earlier [10,11,18], the temperature necessary to generate IBF from these DA products can be accomplished in a toluene solution at about  $110^{\circ}$ C.

## 5. Conclusions

The DA reaction of epoxide 7 and cyclopentadienone 8 forms the exo,endo-adduct 4a and smaller amounts of the exo,exo-product 4b. No products of an endo-attack were isolated. The minor product was isolated in about 6% yield. A detailed investigation of both products found the originally described DAadduct is not the exo,exo-product 4b, but the exo,endo-product 4a. Both structures were confirmed by NMR coupling experiments and X-ray analysis. Thermal analysis revealed the same decomposition pattern with each compound, but the temperature necessary to liberate IBF is  $\approx 60^{\circ}$ C higher in the case of 4b than 4a. As an IBF-precursor, 4a is preferred over 4b for thermally less stable dienophiles.

Based on this investigation, for similar mono and multiple DA adducts of cyclopentadienones with epoxides, the main products will probably have a high amount of exo,endo-configuration and will presumably be less thermally stable than the exo,exo-isomer.

#### Acknowledgements

This work was done when R. Packe-Wirth was at

the Max-Planck-Institut für Polymerforschung. We thank Prof. Dr G. Wegner (Mainz), Prof. Dr A.-D. Schlueter (Berlin) and Dr M. Moukwa (Cleveland) for support of this work, R. Barbour for helpful discussions on the interpretation of the IR spectra, P. Eller for the thermogravimetric measurements and the Bundesministerium für Forschung und Technologie for financial support (Project: planar systems).

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