

Spectral Evidence for γ -EB, a Low-Temperature Modification of Ethyl Benzoate

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A new crystalline modification of ethyl benzoate (γ -ethyl benzoate, γ -EB) has been prepared by deposition of the ester vapour on a cold CsI window. The IR spectrum of the compound is significantly different from the IR spectra of α - or β -EB, in particular the stretching frequency of the C=O group is higher for γ -EB. Two bands of uncertain origin (782 and 341 cm^{-1}) are absent from the spectra of γ -EB and TiCl_4 -EB complexes.

In 1981 Stokr *et al.*¹ published a study on Raman and IR spectra of liquid, solid amorphous, and three crystalline modifications of ethyl benzoate (EB); the three crystalline solids being denoted A, B and C. A was formed by crystallization below ca. -55°C , and B was formed by crystallization at higher temperatures. C was probably formed as a result of contamination with small amounts of moisture. In the present work A and B are denoted α -EB and β -EB, while no name is given for C.

We now report spectral evidence of a new modification, which was obtained by crystallization of the ester vapour from the gas phase onto a cold CsI window close to the temperature of liquid nitrogen. This modification we denote γ -EB.

The results are part of a more comprehensive work on the vibrational analysis of ethyl benzoate and its titanium tetrachloride complexes,² which was a part of a research program on Ziegler–Natta catalysis.³ Earlier we reported a vibrational analysis of ethyl benzoate,⁴ studies of isotopic congeners of ethyl benzoate^{5,6} and the detection of a new ethyl benzoate–titanium tetrachloride complex.⁷ In the near future we will present studies on nine isotopic congeners of ethyl benzoate⁸ and a study on isotopic congeners of titanium tetrachloride complexes.⁹

The aim of these papers is to elucidate fully the vibrational spectra and bonding properties of ethyl benzoate and its complexes. Both the ester and its complexes play a major, but, as yet, unexplained role in Ziegler–Natta catalysis.

Experimental

Fig. 1 gives the experimental set-up for the preparation of the samples. The ester vapour was deposited from a

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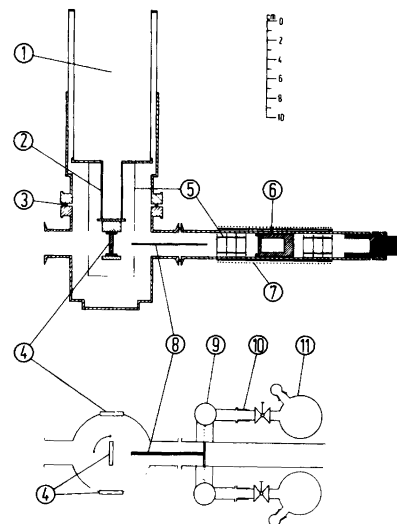


Fig. 1. Experimental set-up for the preparation of samples of ethyl benzoate under vacuum at -196°C . (a) Side view; (b) top view, simplified. 1, Liquid nitrogen container; 2, Cu-tube; 3, O-ring, to allow for twisting of the upper part of the cell; 4, CsI windows; 5, radiation shields; 6–7, Not used in this work; 8, canula; 9, needle valve; 10, glass-metal junction; 11, Schlenk flask with liquid sample.

Schlenk flask (45°C) through a thin canula (0.2 mm inner diameter) with outlet ca. 20 mm from a spectroscopic CsI window. The window was cooled by liquid nitrogen to a temperature approaching -196°C (no independent measurement of temperature was made), and was positioned in a vacuum chamber ($p < 10^{-3}$ Pa). For the preparation of the crystalline samples, the needle valve and the canula were heated to ca. 100°C , and deposition intervals of 30–60 min provided the best results.

The spectra were recorded on a Bruker IFS 113v FTIR instrument equipped with an MCT detector, Ge/KBr beam-splitter and a Globar source. A nominal resolution of

4 cm^{-1} was used, and numerical expansion of the interferogram ensured a peak-position accuracy of $\pm 1 \text{ cm}^{-1}$.

Results and discussion

In Table 1 are given the observed vibrational frequencies for amorphous and crystalline γ -EB, for parent EB and EB- d_5 . The IR spectra are given in Fig. 2. Table 2 is a

Table 1. Comparison of vibrational frequencies (cm^{-1}) for amorphous and crystalline γ -ethyl benzoate.^a

1 EB (am)	2 γ -EB (xl)		3 EB- d_5 (am)	4 γ -EB- d_5 (xl)			
		1-2 ^b			4-3 ^b	3-1 ^b	4-2 ^b
1713	1718	+5	1714	1718	+4		
1603	1604		1602	1603			
1585	1584		1585	1582	-3		-2
1492	1493		1492	1491			-2
1477	1478		1098	1100	+2		
1464	1458	-6	1052	?		c	c
1451	1451		1452	1452			
1444	1445		1048	?		c	c
1393	1398	+5	1198	1199		c	c
1367	1369	+2	1060	1060		c	c
1314	1314		1317	1318		+3	+4
1280	1280		1299	1299		+19	+19
1264	?		936	937		c	c
1176	1180	+4	1177	1178			-2
1159	1162	+3	1158	1159			-3
1125	1131	+6	1124	1127	+3		-4
1110	1114	+4	1098	1100	+2	-12	-14
1100	1099		896	897		c	c
1071	1073	+2	1072	1073			
1028	1028		1026	1026		-2	-2
1010	1013	+3	839	842	+3	c	c
999	1000		1000	1001			
981	977	-4	?	?			
940	942	+2	936	940	+4	-4	-2
877	881	+4	983	981	-2	c	c
853	853		810	811		-43	-42
815	817	+2	592	593		c	c
807	804	-3	809	809		+2	+5
782			777			-5	
712	712		712	712			
688	687		688	688			
675	678	+3	671	673	+2	-4	-5
617	618		617	617			
496	497		483	483		-13	-14
443	445	+2	442	443			-2
?	?		397	?			
392	393		371	371		-21	-22
344			331			-13	
331	337	+6	314	319	+5	-17	-18
272	277	+5	260	265	+5	-12	-12

^aEB(am) = amorphous parent ethyl benzoate, γ -EB(xl) = crystalline parent γ -ethyl benzoate, EB- d_5 (am) = amorphous ethyl benzoate- d_5 , γ -EB- d_5 (xl) = crystalline γ -ethyl benzoate- d_5 .

^b 2-1 and 4-3 = Shifts in frequencies upon crystallization (2-1 = difference between frequencies in column 2 and 1); 3-1 and 4-2 = Isotopic shifts. ^cThe assignments here are somewhat arbitrary as there are severe changes in the description of the vibrations upon deuteration. Therefore no isotopic shifts are given for these vibrations.

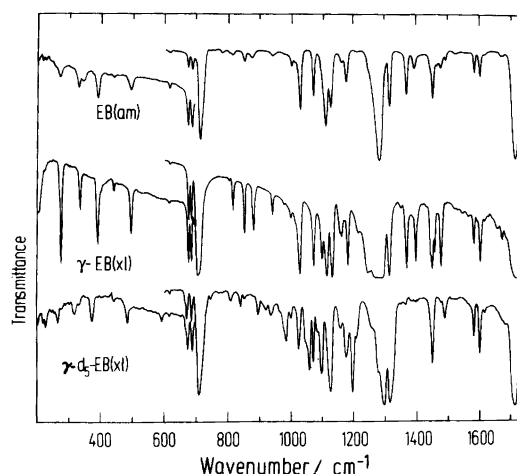


Fig. 2. FTIR spectra of amorphous ethyl benzoate [EB(am)], γ -ethyl benzoate [γ -EB(xl)], and γ -ethyl benzoate- d_5 [γ -EB- d_5 (xl)]. Vibrational frequencies of the most intense bands for γ -EB are taken from the spectrum of a thinner sample.

master table in which the frequencies and IR and Raman intensities are given for all known phases of EB,^{1,4,10} together with data for the equimolar $(\text{TiCl}_4\text{-EB})_2$ complex^{2,9} and calculated frequencies.^{2,4}

The spectrum of the new phase is distinguished from the spectrum of the other crystalline phases in several ways. (i) Whereas in α -EB and β -EB the C=O stretching frequency is lower than for the amorphous ester (1707/1711 cm^{-1} vs. 1713 cm^{-1}), the frequency is higher (1718 cm^{-1}) for γ -EB. (ii) Two bands appearing at 782 and 344 cm^{-1} for the amorphous ester are not observed for γ -EB. The band at 782 cm^{-1} has also been observed by Stokr *et al.*¹ for β -EB, but they were not able to separate the bands at 344/331 cm^{-1} in the IR spectrum. (iii) Several of the bands related to ethyl group vibrations have significantly different intensities when comparing the IR spectra for the individual phases. Differences between the IR spectra of amorphous and γ -EB esters are seen especially in the region 1400–1500 cm^{-1} and at ca. 1100 cm^{-1} (Fig. 2). (iv) The differences between the spectra at ca. 3000 cm^{-1} are striking (Fig. 3), and this region is probably the best part of the spectrum for the identification of γ -EB. Fig. 3 also illustrates the re-

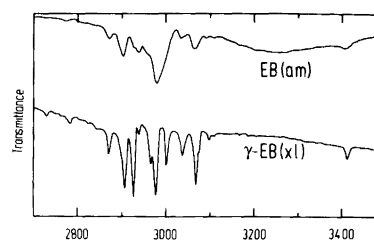


Fig. 3. FTIR spectra of the C-H stretching region of amorphous ethyl benzoate [EB(am)] and crystalline γ -ethyl benzoate [γ -EB(xl)]. The peak at ca. 3410 cm^{-1} is the 1st overtone of the C=O stretching vibration.

Table 2. Overview of observed vibrational frequencies of various phases of ethyl benzoate, with force-field calculations and simplified assignments.^a

Amorph. –196 °C FTIR	Force -field Calc.	Complex ^b –196 °C FTIR	γ-EB –196 °C FTIR	α-EB ^c Raman	β-EB ^c		Liquid 25 °C Raman	Liquid 25 °C FTIR	Vapour 100 °C FTIR	Simplified assignment
					IR	Raman				
1976 w			1996 w 1980 w 1971 w					1966 br i		Overtone 2×999 Combination 981+999
1925 w 1833 w 1793 w			1917 w 1824 w					1916 m i 1817 w		Combination 981+940 Combination 981+853 Combination 940+853
1713 vs i 1673 w	1712	1566 vs	1718 vs 1674 vw 1659 vw	1712/1707	1707	1707	1717 vs vp 1678 w	1720 vs 1679 w 1653 vw	1747 vs 1646 vw	C=O stretch A' Combination 999+675 Combination (?) Combination 999+617
1615 w 1603 m 1585 m 1515 vw		1617 sh	1615 vvw				1615 w			Phenyl Phenyl A' Combination 809+711(?)
1492 w 1477 w 1464 w	1494 1470 1457	1494 w 1468 s 1467 ?	1493 vvw 1478 m 1458 w	1497 1480 1463	1495 1476 1462	1495 1474 1466	1493 w 1479 vw 1458 sh	1492 vw 1477 w 1465 w		Phenyl A' Methylene scissoring A' Methyl antisym. def. A'' Combination 1264+190(?)
1451 m 1444 wsh 1393 m	1456 1452 1399	1452 m 1445 sh 1417 s	1451 m 1445 sh 1398 m	1453 1444 1396/1392	1454 1446 1397	1454 1446 1398/ 1391	1453 m p 1444 sh 1394 m p	1451 m 1444 sh 1393 w	1452 m	Phenyl A' Methyl antisym. def. A' Methylene wag A' Methyl umbrella A' Phenyl A'
1367 m 1314 s	1369 1332	1383 s 1310 s	1369 m 1314 s	1371 1318	1369 1319	1369 1318	1369 m p 1316 m p 1300 vw	1368 m 1314 m	1368 m 1312 m	Combination 853+443(?) α-C–O stretch A' Phenyl A' Methylene twist A''
1280 vs 1264 sh 1246 sh 1212vw	1280 1301 1275	1333 s 1279 w 1252 vw	1280 vs 1254 w 1245 m 1216 w	1272	1288 1271 1252	1286 1272 1250	1276 vs i vp 1264 sh 1246 sh	1277 vs 1246 sh	1277 vs 1248 sh	Combination 853+392 Combination 809+397(?) Uncertain assignment
1176 m	1176	1184 m	1180 m 1170 vvw	1178	1183 1175	1186 1183	1178 s vp	1176 m	1174 m i	Phenyl A' Combination
1159 m i	1153	1164 w 1152 w	1162 w 1155 w	1158 1155	1162 1157	1167 1159	1161 m i p?	1161 sh		Phenyl A' Combination 711+443
1125 s 1110 s 1100 sh 1090 wsh	1123 1111 1103	1170 w 1117 w 1101 w	1131 s 1114 s 1099 m	1125 1112	1128 1112	1128 1112		1119 sh 1109 s 1096 sh	1114 vs i	Skeletal stretch A' Skeletal stretch A' Methyl wag A'' Combination 688+397(?)
1071 m 1028 m 1017 wsh	1074 1029	1075 w 1025 m	1073 m 1028 m	1071 1028	1076 1031	1075 1029	1075 vw 1029 m vp	1070 m 1029 m	1068 m i 1030 m i	Phenyl A' Phenyl A' Combination
1010 w 999 w 999 ^e	1010 1000 998	1010 m 1000 w	1013 sh 1000 w 999 ^e	1003	1003 1003	1003 1003	1010 sh p? 1004 vs vp	1015 sh 1001 w		Ethyl C–C stretch A' Phenyl breath A' Phenyl wag A'' ¹³ C Phenyl breath
981 vw 940 w 877 w 868 wsh 853 m 853 ^{d,e} 815 w 807 sh 782 w 712 vs 688 s 675 s 617 vw 496 2 443 vw 397 ^d 392 w	980 939 880 844 854 816 800 711 686 680 614 497 440 404 402	981 ww 944 vw 864 vw 874 ? 883 vw 846 vw 819 vw 802 vw 711 s 680 w 668 w 615 vw 342 w	977 vvw 942 w 881 m 853 m 817 w 804 vvw 712 vs 687 m 678 m 618 vvw 497 m 445 vw 400 ? 393 m	978 937 883 856 820 807 719 690 676 618 498 442 408 391	989 947 878 868 857 820 808 784 723 691 677 617 498 445 405 395	949 877 866 856 822 810 786 725 691 676 618 497 444 405 396	992 m vp 875 m 853 vs vp 811 vw 808 m 782 m vp 713 vw 685 sh 676 vs p 619 vs p? 497 vw 444 vw 395 vw	937 vw 874 w i 849 w 807 vw i 785 vw 711 vs 688 m i 674 m 618 vw 497 vw 444 vw 398 w	874 w 849 w 680 m i 709 vs 680 m i 614 vw	Phenyl wag A'' Phenyl wag A' β-C–O stretch A' Combination O=C–O scissoring A' Phenyl wag A' Ethyl rocking A'' C=O wag A'' Uncertain assignment Phenyl in-phase wag A'' Phenyl torsion A'' Phenyl in-plane def. A' Phenyl in-plane def. A' Skeletal def. A' Phenyl torsion A'' Phenyl torsion A'' Skeletal def. A'

contd

Table 2. (contd)

Amorph. -196°C FTIR	Force -field Calc.	Complex ^b -196°C FTIR	γ-EB -196°C FTIR	α-EB ^c Raman	β-EB ^c		Liquid 25°C Raman	Liquid 25°C FTIR	Vapour 100°C FTIR	Simplified assignment
					IR	Raman				
344 w br							347 wsh			Uncertain assignment
331 w	321	286 m	337 w	333		333	331 vs vp	332 w i		Skeletal def. A'
272 w	258	231 w	277 m	276		277		272 w		Skeletal def. A'
	213			210/205		204/190	190 vs br	193 w ^g		Skeletal def. A''
	156						158 vw	153 w ^g		Skeletal torsion A''
	129			139		133	120 vvw	118 w ^g		Skeletal torsion A''
	98									Skeletal torsion A''
	91						85 w p?			Skeletal def. A'
	62									Skeletal torsion A''

^aFrequencies in cm⁻¹. Intensities are visual estimates, vs=very strong, s=strong, m=medium, w=weak, vw=very weak, vvw=very very weak. For the polarizations: vp=very polarized, p=polarized and p?=inconclusive observation. i=irregular bandshape, br=broad band, ?=uncertain observation or assignment. Details of the force-field calculation are described elsewhere.^{2,4} ^bCrystalline equimolar (TiCl₄-EB)₂ complex. ^cTaken from Stokr *et al.*¹ ^dObserved for other isotopic congeners, assumed unperturbed. ^eObserved through summation bands. ^fNo observation at this or lower frequencies due to limitations from window materials. ^gTaken from Green and Harrison.¹⁰

duced band-width in the crystalline ester compared with that of amorphous EB.

None of the spectra give evidence of more than one conformer in each of the phases.

The increased C=O stretching frequency may indicate a weaker intermolecular interaction, and the changes in the intensities of the ethyl group vibrations may indicate a change in the conformation of the ethoxy group, although this interpretation is not straightforward.

The disappearance of the bands at 782 and 344 cm⁻¹ is very difficult to explain. The same bands are also absent from the spectra of the TiCl₄-EB complexes,^{2,9} which indicates that the bands are due to some, at present unknown, intermolecular interaction. On the other hand, observed isotopic shifts, force-field calculations, and the apparent lack of the two bands in the spectra of γ-EB and the complexes, indicate that they do not belong to any fundamental. We can offer no plausible explanation in terms of conformational splitting.

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