

STRUCTURE AND MOLECULAR SPECTRA OF ETHYL BENZOATE AND DIETHYL TEREPHTHALATE

Jan ŠTOKR^a, Pavel SEDLÁČEK^b, Danica DOSKOČILOVÁ^a, Bohdan SCHNEIDER^a
and Jan LÖVY^a

^a Institute of Macromolecular Chemistry,

Czechoslovak Academy of Sciences, 162 06 Prague 6 and

^b Chemopetrol, Silon, 391 11 Planá nad Lužnicí

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Infrared and Raman spectra of ethyl benzoate and diethyl terephthalate were measured in their crystalline forms, in the glassy state and in the melt. With liquid samples, the NMR coupling constants ${}^3J_{\text{CH}}$ of the group $-\text{CO.O.CH}_2-$ were also measured. By analysis of these measurements it was found that in the liquid state of ethyl benzoate the following conformers are present: forms with a fully planar structure; forms with the methyl group twisted out of the aromatic and ester group plane by rotation about the $\text{O}-\text{C}_2\text{H}_5$ bond; and forms with non-planar mutual orientation of the ester group and the aromatic ring, formed by rotation about the $\text{C}_{\text{ar}}-\text{CO}$ or $\text{CO}-\text{O}$ bonds. The first two forms are also present in the crystalline modifications of ethyl benzoate. Diethyl terephthalate in the liquid state is present in forms analogous to those of ethyl benzoate; in addition, it contains isomers differing by the mutual orientation of the two ester groups on the aromatic ring.

As part of our studies of the conformational structure of poly(ethylene terephthalate) model compounds, in our previous paper¹ we have investigated the relation between conformational structure and vibrational spectra of methyl benzoate and dimethyl terephthalate; we have discussed the problem of conformer generation in these molecules by rotation about the bonds $\text{C}_{\text{ar}}-\text{C}$, $\text{CO}-\text{O}$, and of the mutual *cis-trans* isomerism of the ester groups of dimethyl terephthalate. In ethyl benzoate and diethyl terephthalate, additional rotations are possible about the $\text{O}-\text{C}_2\text{H}_5$ bond. Complete infrared and Raman spectra of ethyl benzoate have so far been measured in the liquid state²⁻⁶; only in the range of lattice vibrations ($10-200\text{ cm}^{-1}$), Raman spectra have also been measured in the crystalline state⁷. Infrared and Raman spectra of diethyl terephthalate have only been measured in the crystalline state^{5,6,8}. These spectra have been interpreted partly on the basis of analogy with the spectra of similar molecules^{2-4,6,8}, partly by comparison of the experimental band frequencies with the normal vibrations calculated from secular equations⁵. The influence of conformational structure upon vibrational spectra has not been analyzed so far.

By X-ray analysis it was found⁹ that diethyl terephthalate in the crystalline state contains molecules which are essentially planar, with a *trans* mutual orientation of the two ester groups on the aromatic ring. Measurements of dipole moments¹⁰ have indicated that diethyl terephthalate in benzene solution contains approximately equal populations of molecules with *cis* and *trans* mutual orientation of ester groups; for ethyl benzoate a structure with the ester group twisted out of the plane of the aromatic ring¹¹ has been proposed.

In order to refine present data concerning the conformational structure of ethyl benzoate and diethyl terephthalate, and to assign the conformationally sensitive bands in vibrational spectra, we have measured the vibrational spectra of these compounds in the liquid and crystalline states in a broad temperature range. For the determination of the conformational structure of these molecules, use was also made of the measurements and analysis of ^{13}C -NMR spectra of these molecules.

EXPERIMENTAL

Substances

Ethyl benzoate was prepared by reaction of ethanol with benzoyl chloride in the presence of dry pyridine. The product was purified by vacuum rectification on a glass column with Raschig rings (number of theoretical plates for the mixture ethanol-water 2.7), $87^\circ\text{C}/1500\text{ Pa}$; the purity as determined by gas chromatography was better than 99.9%; m.p. -34.5°C . Diethyl terephthalate was prepared by reaction of ethanol with terephthaloyl chloride in the presence of dry pyridine. (Terephthaloyl chloride was prepared by reaction of disodium terephthalate with dry thionyl chloride¹². Disodium terephthalate was prepared by saponification of dimethyl terephthalate by aqueous NaOH). Crude diethyl terephthalate was separated from the reaction mixture in diluted and ice-cooled H_2SO_4 , and further purified by recrystallization from ethanol. The chemical composition of the product was controlled by ^1H -NMR spectra and by elemental analysis (calc.: 64.85% C, 6.4% H; found: 64.4% C, 6.4% H). The purity of the diethyl terephthalate was determined from the melting endotherm on the calorimeter DSC-2 (Perkin-Elmer) according to Plato and Glasgow¹³. The weight of sample was about 1 mg and the purity found 98.8%; m.p. 44.0°C .

Spectra

Infrared spectra were measured on the spectrometers Perkin-Elmer 621 and 580B. Above room temperature, the spectra were measured in a commercial Perkin-Elmer heated cell. Spectra below room temperature, and the dichroism of infrared bands were measured in a special cell of our own construction¹⁴.

Raman spectra were measured on the spectrometer LRDH 800 (Coderg). The spectra were excited by the line 514.5 nm of the Coherent Radiation argon-ion laser. The samples were measured in capillary cells in 90° arrangement. The temperature dependences of Raman spectra were followed in a cell of Harney Miller type¹⁵.

NMR spectra were measured on the spectrometer FX-60 (JEOL) at 15 MHz, equipped with a dual probe suited for the measurement of ^1H and ^{13}C spectra of the same sample in unchanged position. The samples were measured after addition of 20–30% C_6D_6 for establishing the internal lock. The CO band was measured in the range of 1 kHz with 16 K data points (digital resolution 0.125 Hz), using $\pi/4$ pulses and a pulse repetition rate of 20 s, with selective heteronuclear decoupling of the aromatic protons. For the calibration of the irradiation field, the spectrum was measured under identical conditions as the CO band, except for the 2.5 kHz range used in order to measure both the CO and the CH_2 and CH_3 signals in a single run.

RESULTS AND DISCUSSION

Vibrational Spectra of Ethyl Benzoate

Raman and infrared spectra of ethyl benzoate in the liquid and solid states are shown in Figs 1 and 2. Ethyl benzoate solidifies in the glassy state and is difficult to crystallize. Nevertheless, in Raman cells we have been able to prepare, in addition to liquid and glassy samples (Fig. 1*a,b*) also three additional forms which we designate A, B and C; the Raman spectra of these three forms differ, and the bands of lattice vibrations in the range below 200 cm^{-1} indicate some ordering of the molecules of ethyl benzoate (Fig. 1*c,d,e*). Form B is obtained by crystallization in the range -35 to -50°C . Form A is obtained by crystallization at temperatures below -55°C . At temperatures around -50°C this form is transformed to form B. By crystallization in open cells (probably due to contact with atmospheric moisture) we were able to obtain in a part of the sample a third ordered form, designated as C. Besides the liquid and glassy sample, (Fig. 2*a,b*) in infrared cells only a single ordered form could be prepared and measured (Fig. 2*c*). Of the three ordered forms, form A is the

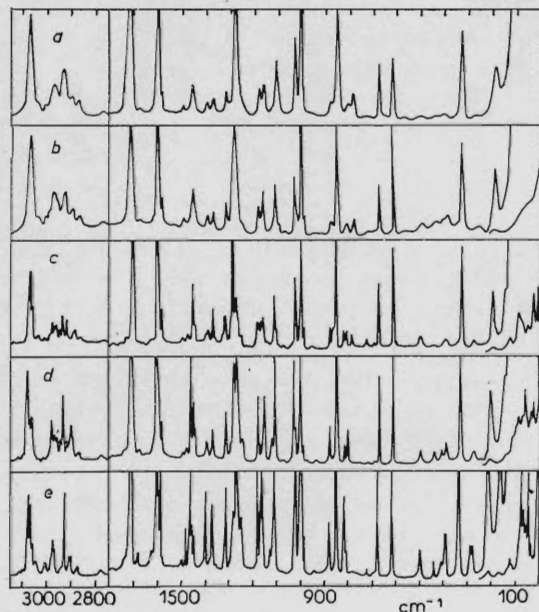


FIG. 1

Raman spectra of ethyl benzoate: *a* liquid, *b* amorphous solid, *c* crystal B, *d* crystal A, *e* crystal C

most important for considerations concerning the conformational structure of ethyl benzoate. In the Raman spectrum of this form (Fig. 1d) as compared to the spectrum of the liquid, the disappearance of the relatively strong band at 784 cm^{-1} and of the very weak band at 555 cm^{-1} is clearly evident. This indicates that the liquid ester contains, in addition to the conformers present in the crystalline form A (conformer I), a further conformer II. A comparison of the intensities of the band at 784 cm^{-1} in Raman spectra of ethyl benzoate measured in liquid and glassy state indicates that the contents of conformer II is smaller in the glassy state than in the liquid. A comparison of the intensities and line shapes in Raman spectra of the liquid and amorphous ester and from the spectrum of the crystalline sample of type A it may be observed, that disappearance of bands upon crystallization occurs not only in the range $780\text{--}820\text{ cm}^{-1}$, but also in the range about $1150\text{--}1185\text{ cm}^{-1}$ and 1420 to

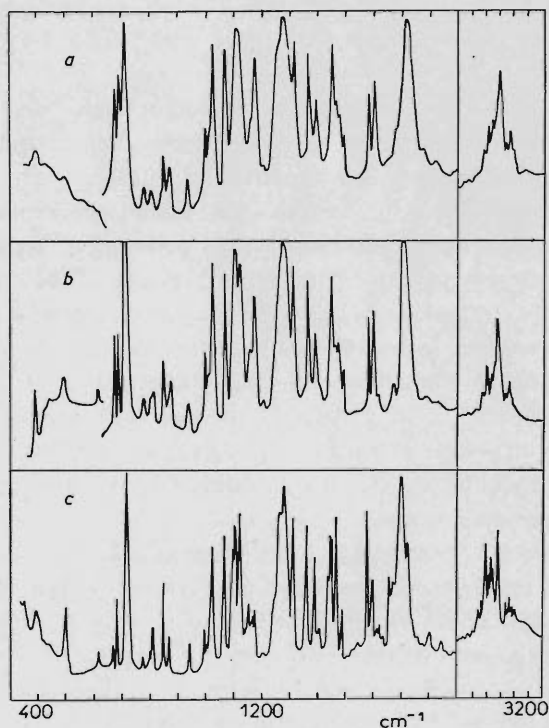


FIG. 2

Infrared spectra of ethyl benzoate: *a* liquid, *b* amorphous solid, *c* crystal B

1500 cm^{-1} . In the latter two ranges, disappearance of bands is less conspicuous because of large band overlap and temperature induced frequency shifts.

The Raman spectrum of the crystalline form C differs very little from the Raman spectrum of form A (Fig. 1e). Bands disappearing upon crystallization into form A, also disappear upon crystallization into form C. The spectra of the forms A and C differ *e.g.* in the doublet which in form A lies at 806 and 820 cm^{-1} , whereas in form C it lies at 817 and 813 cm^{-1} ; the band of form A at 276 cm^{-1} is split into a doublet at 274 and 284 cm^{-1} in form C. We were unable to find out if the crystalline forms A and C differ only by the mutual ordering of the molecules of ethyl benzoate, or if possibly H_2O molecules are incorporated into the lattice in form C.

The Raman spectrum of form B (Fig. 1c) differs profoundly from those of forms A and C. Upon crystallization into form B, only the band at 555 cm^{-1} disappears. Other bands disappearing upon transition from the liquid state into forms A and C, are still present in the crystalline form B. This indicates that in this crystalline form, an additional conformer is present, besides the conformer present in form A.

All the measurements of Raman spectra indicate that liquid ethyl benzoate contains both conformers present in the crystalline forms, plus an additional conformer which is absent in all the three crystalline forms which could be prepared in Raman cells.

With the exception of a very weak band observed in liquid ethyl benzoate (Fig. 2a) at 550 cm^{-1} , no band in the infrared spectrum of ethyl benzoate (Fig. 2c) disappears completely upon crystallization. A comparison of infrared spectra measured in the liquid, glassy and crystalline states indicates that band intensities change profoundly in the ranges 780–830, 1150–1180 and 1440–1500 cm^{-1} . We suppose that these are also conformationally sensitive bands. The presence of these bands in the spectrum of the crystalline sample indicates that in infrared cells we have only succeeded in preparing the crystalline form containing two conformers, similarly as the crystalline form B measured in Raman spectra. This interpretation of the structure of the crystalline form prepared in infrared cells, together with the disappearance of the band at 550 cm^{-1} upon crystallization, is in agreement with the analysis of Raman spectra, according to which the liquid state contains three conformers, two of which also appear in the crystalline state.

Similarly as in methyl benzoate and acetophenone¹, the band of the CO stretching vibration in liquid ethyl benzoate at room temperature is asymmetrical. This asymmetry decreases with increasing temperature and also by dilution with CCl_4 . Contrary to acetophenone and methyl benzoate, this asymmetry is not necessarily explained by intermolecular interactions only, because the band shape can be also affected by the presence of several rotational isomers. The assumption about the effect of rotational isomers is supported by the observation that in a CCl_4 solution of ethyl benzoate, the carbonyl band exhibits almost double the width of the carbonyl band in a corresponding solution of methyl benzoate.

The determination of conformationally sensitive bands and measurement of vibrational spectra in the crystalline state has made possible the refinement of the interpretation of the vibrational spectrum of ethyl benzoate, as presented originally by Boerio and Bahl⁵. This refined interpretation is shown in Table I.

Vibrational Spectra of Diethyl Terephthalate

Raman and infrared spectra of liquid and crystalline diethyl terephthalate are shown in Figs 3 and 4. This ester crystallizes more easily than ethyl benzoate; at room temperature it forms only a single crystalline modification of which the Raman and infrared spectrum could be measured. The frequencies and band widths of some bands of the crystalline sample are sensitive to temperature changes; some of these changes occurring at temperatures below -100°C can be observed in Figs 3 and 4. Upon transition from liquid to crystalline state, band disappearance may be observed both in infrared and in Raman spectra (Fig. 3, 4), indicating the presence of additional conformers in the liquid state. A part of the conformationally sensitive bands is probably connected with the mutual *cis-trans* isomerism of the two ester groups, as described for dimethyl terephthalate¹.

The planar conformer of diethyl terephthalate, with a mutual *trans* orientation of the two ester groups, which is present in the solid state¹⁰, has a centre of symmetry. *cis* Mutual orientation of the ester group leads to disappearance of this centre of symmetry, but causes no other changes in the nearest neighbourhood of the ester group. Similarly as in dimethyl terephthalate¹ it may therefore be expected that the bands sensitive to this type of isomerism will exhibit complementarity in infrared and Raman spectra: at frequencies of infrared bands disappearing upon crystallization, Raman active bands will appear both in liquid and in crystalline samples, and *vice versa*. On the basis of this criterion, the infrared bands (disappearing upon crystallization) at 633, 704, 795, (1174), 1579, (1616), and the Raman bands (disappearing upon crystallization) at 367, 406 and 1410 cm^{-1} can be assigned as bands sensitive to the mutual *cis-trans* orientation of the two ester groups. The wavenumbers of these bands are very near to the wavenumbers of the bands sensitive to mutual *cis-trans* orientation of ester groups in dimethyl terephthalate.

Bands at 335, 468 and 783 cm^{-1} disappear upon crystallization both in infrared and in Raman spectra; at the same time, the band at 783 cm^{-1} corresponds by its behaviour at crystallization and by its depolarization factor in Raman spectra to the band of ethyl benzoate at 784 cm^{-1} . Probably also the bands in the range $1420-1500\text{ cm}^{-1}$ are conformationally sensitive, as their shape and position strongly depend on temperature and crystallization. In Raman spectra of the liquid state, all bands in this range fuse into one broad band; in the infrared spectrum of the liquid state, where four bands may be resolved, the band at 1465 cm^{-1} disappears upon crystallization. Vibrational spectra of the liquid and crystalline samples of diethyl terephthalate in this range are very similar to those of ethyl benzoate.

TABLE I

Interpretation of infrared and Raman spectra of ethyl benzoate. PED designates potential energy distribution, ρ depolarization factor. Experimental wavenumbers which can be assigned to more than one calculated mode, are shown in parentheses

Symmetry	IR		RA	PED		Liquid		Crystal A		Crystal B		
	Calc. ^a	ν , cm ⁻¹		IR	RA	ρ	IR	RA	IR	RA	ν , cm ⁻¹	IR
A'	1 722	1 722	1 724	S(91)		1 721	1 721	0.21	1 712	1 707	1 707	1 707
A'	1 598	1 600	1 605	T(76), ρ (26)		1 604	1 604	0.54	1 604	1 603	1 603	1 604
A'	1 586	1 580	1 585	T(78), ρ (23)		1 586	1 586	0.36	1 586	1 586	1 586	1 586
A'	1 486	1 486	1 495	T(38), ρ (59)		1 493	1 494	0.58	1 497	1 495	1 495	1 495
A'	1 469	1 472	1 470	ψ '(53), ψ (22), α '(19)		1 478	1 478 ^b	—	1 480	1 476	1 476	1 474
A''	1 461	(1 456)		ψ (92)		1 466	—	—	—	(1 462 ^b)	(1 466 ^b)	(1 466 ^b)
A'	1 451	(1 456)		ψ '(37), ψ '(34), α '(19)		(1 453)	(1 453)	(0.57)	1 463	(1 462 ^b)	(1 466 ^b)	(1 466 ^b)
A'	1 448	1 450	1 453	T(37), ρ (50)		(1 453)	(1 453)	(0.57)	1 453	1 457	1 454	1 454
A'	1 369	1 388	1 397	ψ (39), β '(46)		1 447	(1 453)	(0.57)	1 444	1 446	1 446	1 446
A'	1 344	1 362	1 372	β (47), α '(27), β '(13)		1 393	1 393	0.26	1 396	1 397	1 398	1 398
A'	1 324	1 312	1 318	ρ (85)		1 368	1 369	0.30	1 371	1 369	1 369	1 369
A'	1 292	1 280	1 280	T(132)		1 316	1 317	0.30	1 318	1 319	1 318	1 318
A''	1 278			α '(77)		1 278	1 277	0.22	(1 272)	1 288	1 288	1 286
A'	1 262	1 260	1 260	τ_1 (41), θ (21), T '(38)		—	—	—	(1 272)	1 271	1 272	1 272
A''	1 176			β '(34), α '(20), β (24)		1 250	1 252 ^b	—	1 253	1 252	1 252	1 250
A'	1 173	1 171	1 176	ρ (73), T(15)		—	—	—	1 245	—	—	—
A'	1 159	1 158	1 162	ρ (73), T(25)		1 176	1 176	0.33	(1 183)	(1 183)	(1 183)	(1 186)
						1 160	1 161	0.70	(1 183)	(1 183)	(1 183)	(1 186)
						1 155	1 157	—	1 178	1 175	1 183	1 183
						1 158	1 162	—	1 158	1 162	1 162	1 167
						1 155	1 157	—	1 155	1 157	1 157	1 159

A'	1 123	1 108	1 105	$\nu_1(31), \beta'(15), T(13)$	1 124	—	—	1 125	1 128	1 128
A'	1 109	1 068	1 105	$\beta'(25), \nu_2(20), T(10)$	1 110	1 109	0.12	1 112	1 112	1 112
A'	1 073	1 068	1 068	$T(41), \phi(41)$	1 072	1 073 ^b	—	1 071	1 076	1 075
A'	1 037	—	—	$\nu(62), \nu_2(27)$	(1 030)	1 029	0.13	1 034	(1 031)	1 029
A'	1 018	1 025	1 028	$T(38), \phi(29), \Omega(23)$	(1 030)	(1 029)	(0.13)	1 028	(1 031)	1 028
A'	1 000	998	1 002	$T(45), \Omega(34)$	1 003	1 003	0.06	1 003	1 003	1 003
A''	990	—	—	$\mu_1(115)$	—	(991)	(0.3)	(990)	—	(989)
A''	983	—	—	$\mu_1(56), \mu_2(70)$	—	(991)	(0.3)	(990)	—	(989)
A''	931	950	—	$\mu_2(85), \mu_1(33)$	938	—	—	978 ^b	—	—
A'	879	868	871	$\nu_2(45), \beta'(36)$	874	875	0.60	883	947	949
A''	852	(842)	(850)	$\mu_1(64), \mu_2(50)$	—	—	—	—	878	877
A'	843	(842)	(850)	$\nu_1(17), \theta(14), I(16), \nu(17)$	851	852	0.10	856	868 ^b	866 ^b
A''	830	811	820	$\beta(46), \beta'(51)$	820 ^b	816 ^b	—	820	857	856
A''	801	790	793	$\mu_3(35), \mu_1(28), Z(27), M(26)$	807	806	0.50	807	820	822
A''	709	710	—	$\mu_1(93), \mu_2(20)$	785	784	0.10	—	808	810
A''	687	685	—	$Z(94), \mu_3(31)$	711	710 ^b	—	719	784	786
A'	668	672	676	$\Omega(46), T'(13), \theta(14), I(11)$	688	—	—	690	723	725
A'	619	613	620	$\Omega(66), \phi(17)$	675	675	0.10	676	691	691
A'	494	500	502	$\nu(45), \phi(18)$	618	618	0.75	618	677	676
A''	445	448	448	$Z(108), M(52)$	550 ^b	555 ^b	—	—	617	618
A''	409	—	—	$Z(137)$	498	496	0.33	498	—	—
A'	387	392	394	$\nu'(33), \theta(32)$	440	~440	0.5	442	498	497
A'	329	325	332	$\delta(19), T'(16), \Omega(14)$	—	—	—	408	445	444
A'	259	—	—	$\delta(36), \phi(32), \theta(15)$	396	398	0.5	391	405 ^b	408
A''	216	—	—	$\tau_4(95)$	—	333	0.17	333	395	396
A''	169	—	—	$M(40), Z(26)$	—	278	0.4	276	—	277
					—	(190)	(0.75)	210	—	204
					—	(190)	(0.75)	205/139	—	190/133

^a Data from ref. 5; ^b Poorly defined lines.

TABLE II

Interpretation of infrared and Raman spectra of diethyl terephthalate. PED designates potential energy distribution, ρ depolarization factor. Experimental wavenumbers which can be assigned to more than one calculated mode, are shown in parentheses

Symmetry	IR		PED		Liquid		ρ	Crystal I		Crystal II	
	Calc. ^a	RA	RA	PED	IR	RA		IR	RA	IR	RA
	ν, cm^{-1}				ν, cm^{-1}			ν, cm^{-1}		ν, cm^{-1}	
A_g	1 723	1 724	S(90)		1 725	0.20	1 734	1 727	1 734	1 727	1 747
							1 718	1 732	1 718	1 732	1 732
B_u	1 721	1 719	S(93)		1 724			1 728		1 719	1 724
								1 719		1 713	1 711
A_g	1 606	1 614	T(73), $\varphi(24)$		1 615 ^c	0.45	1 614	(1 615 ^b)	1 614	(1 615 ^b)	1 615
											1 606
A_g	1 585	1 581	T(91), $\varphi(12)$		1 579 ^c	0.3	1 579	(1 577 ^b)	1 578	(1 573 ^b)	1 579
								(1 570 ^b)			
B_u	1 507	1 500	$\varphi(50)$, I(38)		1 507			1 505		1 504	
B_u	1 470		$\psi''(51)$, $\psi'(24)$, $\alpha'(19)$		1 478	0.2		1 476		1 481	
					1 468						
A_g	1 469	1 463	$\psi''(52)$, $\psi'(24)$		1 475 ^b	0.2			1 476		1 479
B_g	1 461	1 457	$\psi''(92)$		(1 453)	(0.63)			1 458		1 471
A_u	1 461	1 452	$\psi''(92)$		(1 449)					1 461	
A_g	1 452	1 451	$\psi''(40)$, $\psi'(36)$		(1 453)	(0.63)			1 447		1 442
B_u	1 452		$\psi'(41)$, $\psi'(35)$, $\alpha'(19)$		(1 449)				1 450		1 446
B_u	1 426	1 408	T(37), $\varphi(29)$, $\vartheta(16)$		1 410	0.21			1 411		1 407
A_g	1 376	1 398	$\beta(21)$, $\vartheta(19)$, $t_1(13)$, $T'(14)$, $\beta'(13)$		1 395	0.24			1 393		1 394
									1 384		1 382
B_u	1 371	1 388	$\beta'(42)$, $\psi''(35)$		1 393				1 393		1 394
A_g	1 365	1 363	$\beta'(39)$, $\psi''(33)$		1 369	0.21			1 363		1 364
B_u	1 350	1 362	$\beta'(25)$, T(16), $\varphi(13)$, $\beta'(15)$, $\alpha'(14)$		1 369				1 374		1 373
									1 363		1 363

A_g	1 333	1 308	$\beta'(42), \alpha'(28)$	1 305	0-15	1 303	1 303	1 303
B_u	1 324	1 318	$T(37), \beta(22), \theta(17), \varphi(15), \alpha'(16) \sim 1306$	1 322		1 322	1 323	1 289
A_g	1 293	1 285	$\varphi(64), t_2(13)$	1 278	0-15	1 283		1 284
B_u	1 279	1 270	$T(106)$			1 276	1 269	
B_g	1 277		$\alpha'(77), \beta(32)$			1 268		1 233
A_u	1 277		$\alpha'(77), \beta(32)$			1 246	1 246	1 265
A_g	1 179	1 174	$\varphi(72), T(15)$	1 252	0-11	1 170		1 170
B_g	1 175		$\beta'(34), \alpha'(20), \beta(24)$	(1 174 ^c)		1 192		1 193
A_u	1 175		$\beta'(34), \beta(24), \alpha'(20)$	(1 174)		1 160	1 177	1 187
B_u	1 132		$\Omega(25), \varphi(21), t_1(20), T'(16)$	1 023		1 131	1 162	
A_g	1 122	1 125	$T(30), t_1(30)$	(1 105)	(0-10)		1 130	
B_u	1 115	1 110	$\beta'(38), r(12), \gamma'(13), t_2(13)$	1 114 ^b		1 113	1 114	(1 104)
A_g	1 114		$\beta'(31), t_2(17), T(13)$	(1 105)	(0-10)			(1 104)
B_u	1 103		$\varphi(56), T(33)$	1 104		1 104	1 106	
A_g	1 037	1 024	$r(62)$	1 017	0-37	1 019		1 024
B_u	1 037		$r(63), t_2(29)$	(1 021)			(1 024)	1 021 ^b
B_u	1 019	1 015	$\Omega(39), T(27), \varphi(26)$	(1 021)			(1 024)	
A_u	991	975	$\mu_2(125)$	971		979	979	969
B_g	972	975	$\mu_2(135)$					883
A_g	888	882	$t_1(35), \beta'(19)$	877	0-4	879	873	
B_u	885	870	$\beta'(31), t_1(27), t_2(22)$	(876)		(873)		864
A_g	875	860	$t_2(42), \beta'(17)$	(876)	0-06	861	881	
A_u	871	872	$\mu_2(85)$	(876)		(873)	881	
B_u	863	842	$t_2(32), t_1(13), r(20)$	845		843	845	

TABLE II
 (Continued)

Symmetry	IR		PED	Liquid		Crystal I		Crystal II	
	Calc. ^a	RA		IR	RA	IR	RA	IR	RA
	ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}
B_g	859		$\mu_2(114)$				840 ^b		841
B_g	831		$\beta'(52), \beta(47)$		816 ^b		816		818
A_u	828	813	$\beta'(55), \beta(51)$	816 ^b		816		817	
B_g	799		$Z(44), \mu_3(42), M(37)$	795 ^c	794	793			794
A_u	727	722	$\mu_2(45), \mu_3(59)$	783	783				
A_g	724		$\Omega(38), T'(27), T(16), \theta(12)$	731	732 ^c	727		726	708
B_g	674		$Z(87)$	704 ^c	704		705		676
A_g	627	631	$\Omega(63), \phi(16)$	633 ^c	633	633	634		631
				535					628
B_u	529	502	$T'(37), \theta(24), \gamma(19)$	503		504		504	518
A_g	521		$\gamma(39), \phi(30)$		520		519		
A_u	471		$M(80), Z(89)$						
B_u	443	450	$\gamma(35), \gamma'(27)$	468	470 ^b				
				451 ^b					
A_u	411		$Z(135)$	405	406 ^c	451		450	
A_g	392		$\gamma'(40), r(14), \delta(13)$		406 ^c	406 ^c	385		382
B_u	367	362	$\delta(30), \gamma'(19), r(15)$	365	367 ^{b,c}	363			
				333	338				
A_g	289		$\phi(37), \delta(27), \gamma'(17)$		~270				302 ^b
									288
A_g	250	254	$\Omega(19), \delta(22), T'(21)$		~251	~0.2	286		250
B_g	247		$M(73)$		~240	~0.5	250		245

^a Data from ref.⁵; ^b poorly defined lines; ^c bands assigned to the form with mutual *cis* orientation of the two ester groups.

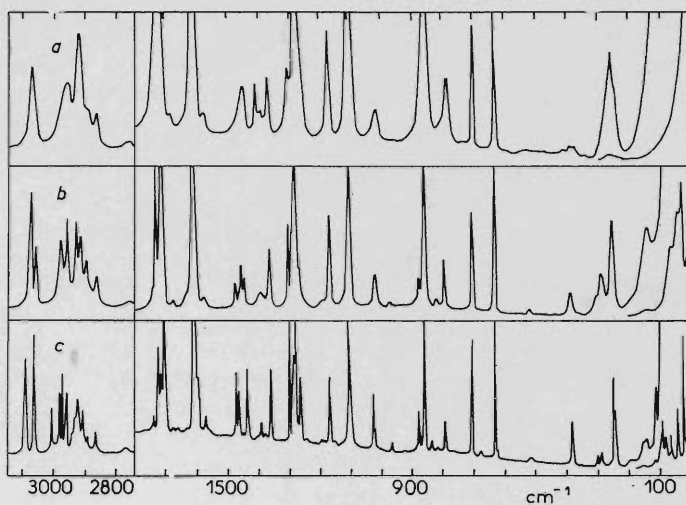


FIG. 3

Raman spectra of diethyl terephthalate: *a* melt, *b* crystal at 30°C, *c* crystal at -140°C

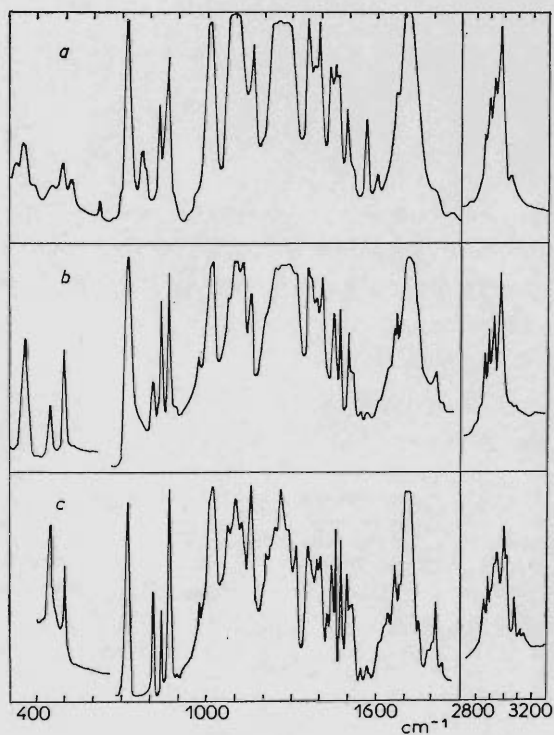


FIG. 4

Infrared spectra of diethyl terephthalate: *a* melt, *b* crystal at 30°C, *c* crystal at -100°C

Infrared spectra of liquid diethyl terephthalate exhibit a prominent band at 535 cm^{-1} which disappears upon crystallization. Both its position, and the fact that a corresponding band is missing in the Raman spectrum, are reminiscent of the band at 529 cm^{-1} in infrared spectra of dimethyl terephthalate, which has been interpreted as a band sensitive to isomerism created by rotation about the bond $\text{C}(\text{:O})\text{—O}$ or $\text{C}_{\text{ar}}\text{—CO}$. It is probable that the band at 535 cm^{-1} in infrared spectra of liquid diethyl terephthalate is also sensitive to this type of isomerism.

Determination of the effects of rotational isomerism upon vibrational spectra of diethyl terephthalate together with the measurement of spectra of liquid samples has made possible the refinement of the interpretation of infrared and Raman spectra of this ester⁵ as measured both in the liquid and in the solid state (Table II).

For analysis of conformational structure generated by rotation about $\text{O—C}_2\text{H}_5$ bond, use was made of the NMR coupling constant ${}^3J_{\text{CH}}$ of the fragment —CO.O.CH_2 (further designated as J_{e}), as determined by analysis of the carbonyl signal in ${}^{13}\text{C}$ -NMR spectra measured with selective heteronuclear decoupling of the aromatic protons. The relation between this coupling constant measured in the presence of the irradiating field of intensity $H_2(J_{\text{eR}})$ and the real value (J_{e0}) is given by the equation^{16,17}

$$J_{\text{eR}} = [(\Delta\nu - \frac{1}{2}J_{\text{e0}})^2 + (\gamma H_2)^2]^{1/2} - [(\Delta\nu + \frac{1}{2}J_{\text{e0}})^2 + (\gamma H_2)^2]^{1/2}, \quad (1)$$

where $\Delta\nu$ is the difference of the resonance frequency of the proton interacting with the measured carbon and of the irradiation frequency. The intensity of the irradiating field H_2 was determined by means of the ${}^1J_{\text{CH}}$ coupling constants of the CH_3 and CH_2 group carbons, measured with and without irradiation of the aromatic protons.

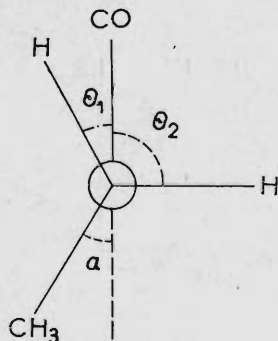


FIG. 5
Designation of the angles α , θ_1 and θ_2 in the group $\text{CO.O.C}_2\text{H}_5$

Both for ethyl benzoate, and for diethyl terephthalate, at γH_2 139 ± 5 Hz, $J_{eR} = 2.56$ Hz, equal for the two esters within the limits of the digital resolution 0.125 Hz. In the limits of this resolution the corrected values (J_{e0}) were 3.0 Hz.

Similarly for methyl benzoate, the value J_{eR} 3.42 Hz was found at $\gamma H_2 = 142$ Hz, yielding the corrected value J_{e0} 4.0 Hz, in very good agreement with the value found previously for an analogous coupling constant in methyl acetate¹⁸.

For the determination of conformational structure from the value of ${}^3J_{CH}$, the dependence of this coupling constant on the dihedral angle Θ between the coupled nuclei (Fig. 5) has to be known. Both theoretical and experimental data in the literature^{19,20} indicate that in the fragment studied by us, a Karplus type²¹ dependence may be assumed to exist; exact parameters of this dependence are not available. Therefore our analysis was based a) on the simplest equation

$$J = A \cos^2 \Theta, \quad (2)$$

according to which the coupling constants for the angles Θ 180° (J_T) and Θ 60° (J_G) are in the relation $J_T = 4J_G$, and b) on the theoretical equation¹⁹

$$J = 4.26 - 1.00 \cos \Theta + 3.56 \cos 2\Theta \quad (3)$$

according to which $J_T = 4.4J_G$. In both procedures, the value J_{e0} was normalized by means of the experimental value for methyl benzoate using the relation $J_{e0} = (1/3)(J_T + 2J_G) = 4.0$ Hz. Equation (2) then yields $J_G = 2.0$ Hz, $J_T = A = 8.0$ Hz; equation (3) yields $J_G = 1.9$ Hz, $J_T = 8.3$ Hz.

The vicinal coupling constant ${}^3J_{CH}$ in NMR spectra can be applied to the determination of conformational structure only if the studied substance is present as a single conformer; otherwise the found value of ${}^3J_{CH}$ is the weighted average of the values for all the conformers present. The assumption of the presence of a single conformer on the O—C₂H₅ bond (or rather of two equienergetic mirror image forms) in ethyl benzoate and diethyl terephthalate yields, based on equation (2)

$$\frac{1}{2}(\cos^2 \Theta_1 + \cos^2 \Theta_2) = \frac{J_{e0}}{A} = \frac{3.0}{8.0} = 0.375; \quad (4)$$

as $\Theta_1 - \Theta_2 = 120^\circ$, this result corresponds to a form with the CH₂ group protons oriented at Θ_1 30° and Θ_2 -90° with respect to the plane of the ester group, *i.e.* with the methyl group twisted by α 30° from this plane (Fig. 5). Based on the theoretical equation (3), α would be greater by about 5° . Under the assumption of the presence of two conformers, one with a *trans* orientation of the methyl group, and of the

other with the methyl group twisted out of the plane by the angle α , we obtain

$$J_{e0} = p_t J_G + p_x \frac{J_{\alpha+120} + J_{\alpha-120}}{2}; \quad p_x = p_{\alpha_1} + p_{\alpha_2} \quad (5)$$

$$p_t + p_x = 1.$$

For $\alpha 60^\circ$, equations (2) and (3) yield the contents of the *trans* form (p_t) 0.67, for $\alpha 90^\circ$ equation (2) yields p_t 0.75, equation (3) yields p_t 0.70. In the sense of the expression

$$p_t = \exp(\Delta G/RT)/[2 + \exp(\Delta G/RT)] \quad (6)$$

the free energy difference ΔG between the *trans* form and both mirror image forms with the out-of plane orientation of the methyl group is approximately 3.4 kJ/mol for $\alpha 60^\circ$ and $\Delta G \approx 4$ kJ/mol for $\alpha 90^\circ$.

Conformational Structure of the Esters

Information about the conformational structure of ethyl benzoate and diethyl terephthalate in the crystalline and liquid states can only be obtained by combination of the results of analysis of vibrational and NMR spectra, with X-ray data on the structure of crystalline diethyl terephthalate and with our knowledge of the conformational structures of methyl benzoate and dimethyl terephthalate.

Analysis of $^3J_{CH}$ coupling constants in NMR spectra indicates that the carbons of the $-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_3$ group have the same geometrical arrangement in both studied esters; this arrangement can either be described by a single nonplanar structure of this group, in which the methyl groups are twisted out of the plane by rotation about the $\text{O}-\text{C}_2\text{H}_5$ bond, or by a combination of two or more rotamers differing by the angle of rotation about the $\text{O}-\text{C}_2\text{H}_5$ bond.

Analysis of vibrational spectra indicates the presence of three different types of conformational structure in ethyl benzoate: type *I*, which is present in all crystalline forms and in the liquid sample; type *II* which is present in the crystalline form **B** and in the liquid; and type *III* which is only present in the liquid. Diethyl terephthalate in the crystalline state has a totally planar structure with a mutual *trans* orientation of the ester groups (conformer *I*); in addition to the bands of conformer *I*, in the liquid state there also appear bands of the form with a *cis* mutual orientation of the two ester groups, as well as bands corresponding to the conformational types *II* and *III* of ethyl benzoate. The band of the ethyl benzoate conformer *III* at 555 cm^{-1} , and the corresponding band of ethyl terephthalate at 534 cm^{-1} both have the same shape and intensity as the analogous bands of methyl benzoate and dimethyl terephthalate which are characteristic of a nonplanar conformation, with the ester group twisted out of the plane of the aromatic ring, either by rotation about the $\text{C}_{ar}-\text{CO}$ or the

C(:O)—O bond. The bands of conformer *II* which have no analogy in methyl benzoate or dimethyl terephthalate, are assumed to be characteristic of a conformer differing by rotation about the O—C₂H₅ bond. All bands characteristic of conformer *II* of ethyl benzoate are also observed in the spectra of liquid diethyl terephthalate. The finding that liquid diethyl terephthalate contains, in addition to the form with the planar arrangement of the atoms C—O—CH₂—CH₃, a further conformer differing by rotation about the O—C₂H₅ bond, gives preference to the interpretation of NMR spectra based on the assumption of the presence of two conformers differing by rotation about the O—C₂H₅ bond. Even though the angle of rotation about the O—C₂H₅ bond is not exactly known for the second conformer, analysis of NMR spectra indicates a strong predominance of the form with the *trans* position of the methyl group, with the free energy difference between these two forms in the range 3.4 to 4 kJ/mol.

All the results may be summarized as follows: In all crystalline forms of ethyl benzoate, the aromatic ring and the ester group are coplanar. It is possible to prepare a crystalline form of ethyl benzoate containing two conformational forms: one totally planar, and the other with the methyl group twisted out of the plane by rotation about the O—C₂H₅ bond. In the liquid there appears a third conformational structure, differing by rotation either about the bond C_{ar}—CO or C(:O)—O. Liquid diethyl terephthalate contains the same forms of the —CO—CH₂—CH₃ group as ethyl benzoate; in addition, it contains conformers differing by the mutual orientation of the two ester groups.

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