

STRUCTURE AND VIBRATIONAL SPECTRA OF METHYL BENZOATE AND DIMETHYL TEREPHTHALATE

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Infrared and Raman spectra of the crystalline forms and of the liquid state of acetophenone, methylbenzoate and dimethyl terephthalate were measured. From these measurements it was found that acetophenone in the liquid state is present in a single conformational form, and that methyl benzoate in the liquid state contains, in addition to the major conformer with a planar structure and *trans* form of the ester group, also a minor conformer of different geometrical structure. Dimethyl terephthalate in the melt contains approximately equal populations of the conformers with the mutual *trans* and *cis* orientation of the two ester groups. For all the observed structures, the conformationally sensitive bands were assigned.

Methyl benzoate and dimethyl terephthalate are the simplest models used in studies of the vibrational spectra of poly(ethylene terephthalate)¹. Probably for this reason, the vibrational spectra of these compounds have been much studied in the past. Bands in infrared and Raman spectra of these molecules have been interpreted on the basis of known group frequencies of similar molecules²⁻⁶. These empirical assignments have been refined by calculations of normal frequencies from secular equations^{7,8}. In both these molecules, formation of rotational isomers can take place. So far vibrational spectra have not been used for the investigation of the existence of such rotational isomers, and of their possible effects upon vibrational spectra.

In this paper we have tried, by the measurement of infrared and Raman spectra of liquid and crystalline samples of methyl benzoate and dimethyl terephthalate, to investigate the effect of rotational isomerism upon vibrational spectra of these compounds. As in this type of substances, the spectra may be affected by intermolecular interactions, we have also measured vibrational spectra of liquid and crystalline acetophenone.

EXPERIMENTAL

Chemicals

Acetophenone, chemically pure (Soyuzexport, Moscow) was rectified on a glass column filled with Raschig rings (number of theoretical plates for a mixture ethanol-water 2.7) at 87°C/2150 Pa; purity of product 99.7% (by chromatography); m.p. 20.5°C. Methyl benzoate was prepared by the

reaction of benzoyl chloride with methanol (both compounds of *p.a.* purity, Lachema, Brno) and purified by vacuum rectification on the same column as acetophenone, at 85°C/2000 Pa; purity of product 99.9% (by chromatography); m.p. -12.5°C. Dimethyl terephthalate (Dynamit-Nobel) was of 99.8% purity (by melting endotherm on the calorimeter DSC-2, Perkin-Elmer); m.p. 141.5°C.

Spectral Measurements

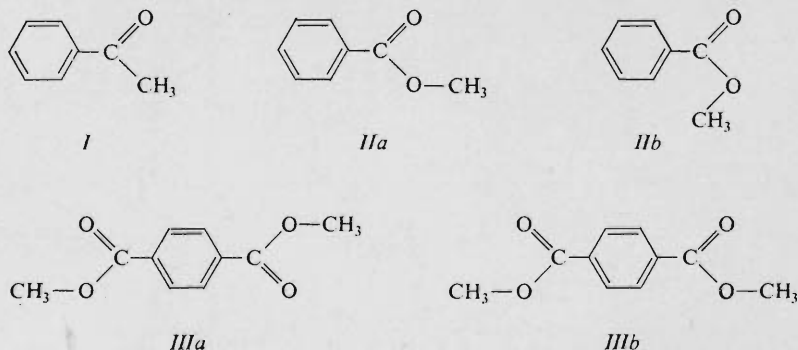
Infrared spectra were measured on the spectrometers PE 621 and 580 B. Above room temperature the spectra were measured in the commercial Perkin-Elmer heated cell. At and below room temperature, and for the determination of dichroic ratios of infrared bands, the spectra were measured in a special cell of our own construction⁹.

Raman spectra were measured on the spectrometer LRDH 800 (Coderg). The spectra were excited by the line 514.5 nm of the argon-ion laser (Coherent Radiation Co.). The samples were measured in capillary cells in 90° arrangement. Some spectra were recorded by means of the computer PDP 11-05 in Tracor system. The temperature dependences of the Raman spectra were determined in a cell of Harney Miller type¹⁰.

RESULTS AND DISCUSSION

Acetophenone

X-ray diffraction studies have shown¹¹ that the molecule of acetophenone (*I*) is planar in the crystalline state (Scheme 1). In the liquid state, rotation of the phenyl group about the C_{ar}-C bond could lead to the formation of rotational isomers.



SCHEME 1

In transition from the liquid to the solid state, disappearance of bands is observed neither in the infrared (Fig. 1) nor in the Raman spectra (Fig. 2) of this compound, indicating that no rotational isomers are formed. Therefore it may be assumed that in the liquid state the molecule of acetophenone is planar, similarly as in the solid state¹¹. Spectra of crystalline acetophenone, compared with those of the liquid,

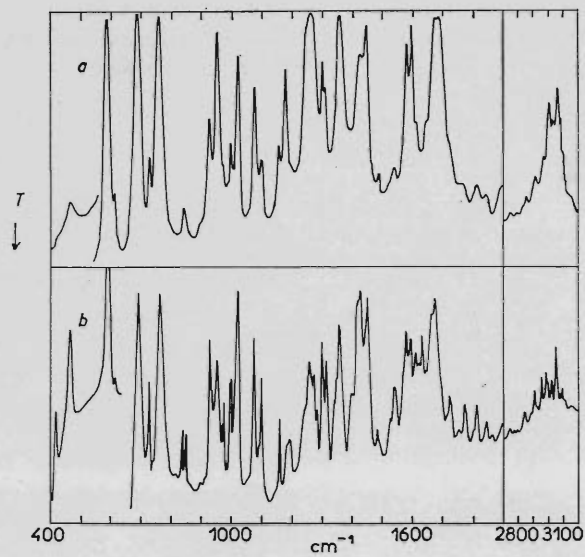


FIG. 1
Infrared spectra of acetophenone: *a* liquid, *b* crystal

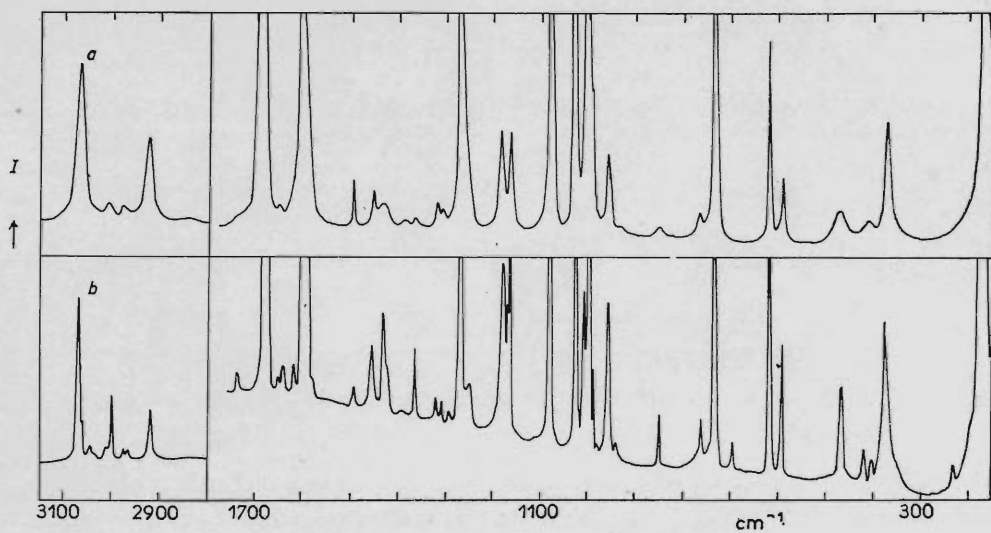


FIG. 2
Raman spectra of acetophenone: *a* liquid, *b* crystal

exhibit splittings or intensity changes of some bands. Such changes are prominent *e.g.* on the Raman bands at 160–180, 230, 408, 690, 848, 1291, 1360, 1430 and 1490 cm^{-1} , and on the infrared bands at 840–850, 970–980 and 1240–1290 cm^{-1} . The shape and intensity of some bands in infrared spectra of crystalline samples depends on the cooling procedure. Measurements of the dichroism and of the tilting effect have shown that these differences are only given by the orientation of the crystals in the cell. Interesting is the behaviour of the carbonyl band. In the liquid state in the Raman spectrum this is broad and asymmetrical. In dilute solution the carbonyl band is narrower and symmetrical. Also with increasing temperature in the liquid state the band becomes narrower and more symmetrical. This change of the carbonyl band shape indicates interaction and formation of associates of the acetophenone molecules in the liquid state; these associates are destroyed upon dilution. A broadening and asymmetry of bands caused evidently by association may also be observed on the band of the methyl group stretching vibration.

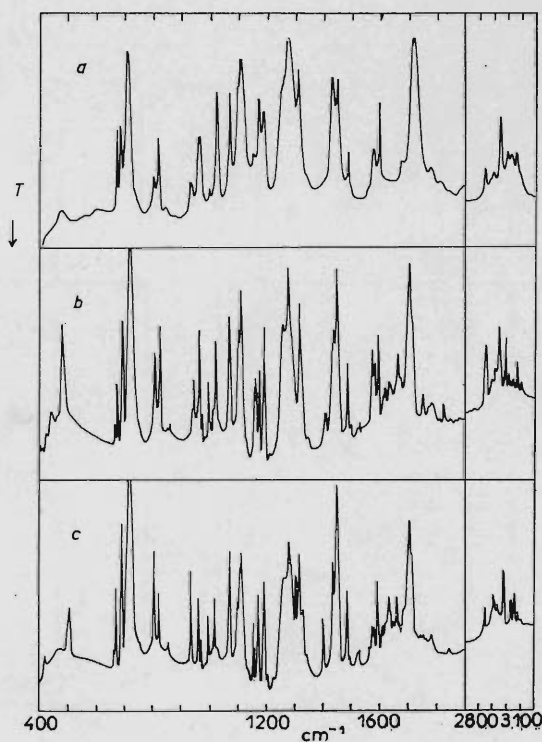


FIG. 3
Infrared spectra of methyl benzoate: *a* liquid, *b* crystal A, *c* crystal B

Methyl Benzoate

According to X-ray analysis¹² the molecule of methyl benzoate (*II*) measured in the complex with $\text{Cr}(\text{CO})_3$ is planar, with a *trans* orientation of the CH_3 group (*IIa*). In the liquid state, rotational isomers may be formed by rotation about the $\text{CO}-\text{O}$ (*IIb*) and $\text{C}_{\text{ar}}-\text{C}$ bonds. The formation of rotational isomers by rotation about the $\text{CO}-\text{O}$ bond has been proved for some esters¹³.

In infrared (Fig. 3) and Raman spectra (Fig. 4) we were able to differentiate two crystalline forms, further designated as forms A and B. Form A is formed by crystallization from supercooled liquid samples. It is transformed to crystalline form B in the vicinity of the melting point. Raman spectra of these two crystalline forms differ only by the position of the band of the in plane bending vibration of the ester group at 485 cm^{-1} in form A and at $505-510\text{ cm}^{-1}$ in form B; by the position of the band of the in plane bending vibration at 340 cm^{-1} in form A and at 328 cm^{-1} in form B; by the position of the band of the torsional vibration of the CH_3 group

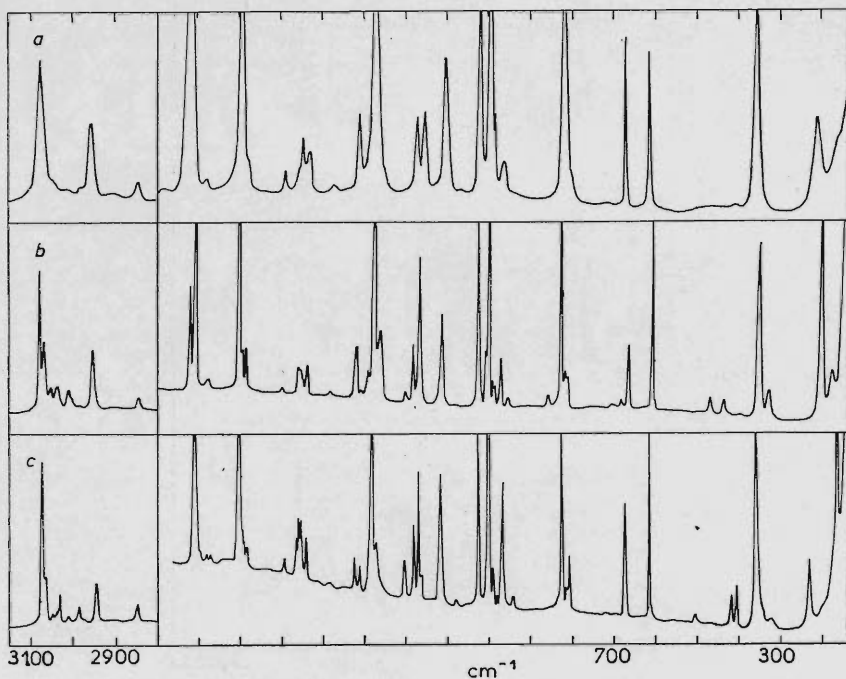


FIG. 4

Raman spectra of methyl benzoate: *a* liquid, *b* crystal A, *c* crystal B

at 216 cm^{-1} in form A and at 236 cm^{-1} in form B; and by the position of the band of the torsional vibration of the benzene ring skelet at 447 cm^{-1} in form A and at 421 cm^{-1} in form B. Further differences between the spectra of the crystalline forms A and B are observed on the bands of the benzene CH bending vibrations where in infrared spectra form A exhibits a singlet at 1319 cm^{-1} and form B exhibits a triplet at $1308, 1320$ and 1333 cm^{-1} . The remaining bands exhibit only minor differences of band intensities and positions which are probably caused by crystalline splitting of bands. The spectra of liquid samples are similar to those of the crystalline form A, except for the differences caused by crystalline splitting and by band widths. In addition, both the infrared and the Raman spectrum of the liquid exhibits a very weak band of the bending vibration of the ester group at 510 cm^{-1} which is also observed in the spectrum of the crystalline form B. This indicates that the crystalline forms A and B correspond to different conformational forms of methyl benzoate. The major component in the liquid state has the same conformational structure as the crystalline form A. For this conformer we assume the same structure as was found by X-ray analysis (IIa). The liquid also contains a minor component, of the same conformational structure as that appearing in the crystalline form B. In agreement with this interpretation, in the liquid the intensity of bands corresponding

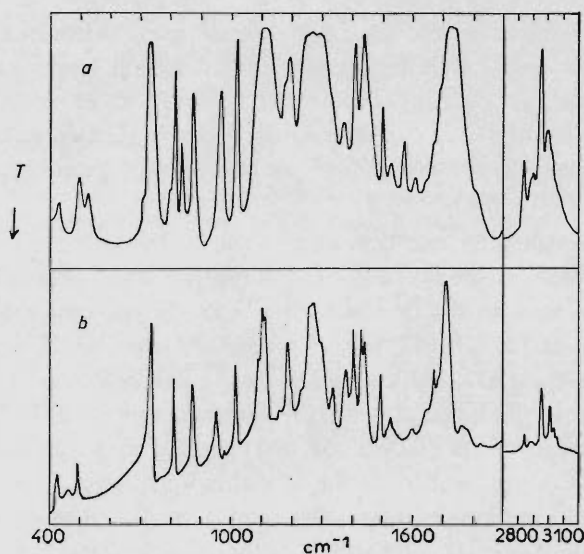


FIG. 5
Infrared spectra of dimethyl terephthalate: *a* melt, *b* crystal

to the crystalline form B increases with temperature. The conformational structure of the minor component cannot be directly determined from vibrational spectra. As no rotational isomers have been detected in acetophenone, it may be assumed that the conformer appearing in the crystalline form B, differs from that of the crystalline form A by rotation about the CO—O bond (*IIf*); however, the possibility of a rotation about the C_{ar}—C bond cannot be completely excluded.

Similarly as with acetophenone, also with methyl benzoate an influence of intermolecular interactions upon vibrational spectra can be expected. This is very pronounced on the shape of the band of the C=O stretching vibration. In Raman spectra of the liquid, the carbonyl band is broad and asymmetrical. An increase of temperature, and especially dilution of the sample by CCl₄ lead to symmetrization and narrowing of this band.

In the vibrational spectra of methyl benzoate measured by us we have detected some previously not interpreted bands. We have based their interpretation on a comparison of the experimental wavenumbers with those calculated by Boerio and Bahl⁸ from secular equations. An interpretation of the ranges of these new bands (1486–1324, 1000–620, 480–360 cm⁻¹) is summarized in Table I.

Dimethyl Terephthalate

In dimethyl terephthalate, rotational isomers can be formed by rotations about the same bonds as in methyl benzoate. In addition, rotational isomers differing by the mutual orientation of the two ester groups may also appear. It has been shown by X-ray analysis¹⁴ that the molecule of dimethyl terephthalate is planar in the crystalline state, with a *trans* conformation of the ester groups on the aromatic ring (*IIIa*). In the liquid state, measurements of dipole moments have indicated¹⁵ the presence of a considerable amount of molecules with a mutual *cis* orientation of the two ester groups (*IIIb*).

This ester appears in only one crystalline form¹⁴. In both the infrared spectra (Fig. 5) and in the Raman spectra (Fig. 6), disappearance of bands is observed upon transition from the melt to the crystalline state; in the infrared spectrum the disappearing bands lie at 1577, (965), 837, 796, 633, 529 and 350 cm⁻¹, in the Raman spectrum at 1409, 1113, 812, (730) and 327 cm⁻¹. This indicates that several conformers are present in the liquid state. With one exception (529 cm⁻¹), all the conformationally sensitive bands (*i.e.* bands disappearing upon crystallization) have the property that the wavenumbers of the conformationally sensitive infrared bands correspond to conformationally insensitive bands in the Raman spectrum, and *vice versa* (Fig. 5, 6, Table II). This indicates that the conformers present in the liquid state exhibit vibrational modes at equal wavenumbers which differ only by the activity of bands in infrared and Raman spectra. Such character of infrared and Raman spectra can be expected for the conformers differing by mutual orientation of the

TABLE I

Interpretation of some parts of infrared and Raman spectra of methyl benzoate. PED designates "potential energy distribution". Wavenumbers which can be assigned to more than one vibrational mode are given in parentheses

Symmetry	Calculation ^a	ν, cm^{-1}		PED		Liquid		Crystal A		Crystal B	
		IR	RA	IR	RA	IR	RA	IR	RA	IR	RA
A'	1 486	1 492	1 495	T(37), φ (59)		1 494	1 495	1 492	1 495	1 492	1 495
A'	1 461			α (66), ψ (52)					1 459		1 464
A'	1 448	1 451	1 455	T(39), φ (53)		1 453	1 454	1 453	1 453	1 454	1 458
A'	1 437	(1 434)	(1 438)	ψ (71), α (27)		(1 436)	(1 437)	(1 440)	1 447	(1 440)	1 450
A''	1 434	(1 434)	(1 438)	ψ (74), α (25)		(1 436)	(1 437)	(1 440)	1 434	(1 440)	1 440
A'	1 324	1 313	1 317	φ (89)		1 316	1 317	1 319	1 321	{ 1 332 1 320	{ 1 324 1 313
A'	1 000	1 000	1 004	T(43), Ω (36)		1 003	1 003	1 002	1 003	1 002	1 004
A''	980			μ_1 (115)		992	991		990	989	991
A''	983		970	μ_2 (70), μ_1 (33)				982	984	977	980
A'	954	963	968	t_2 (86)		967	969	970	972	970	969
A''	930	934		μ_2 (85), μ_1 (33)		938	937	946	944	942	944
A''	852	850	851	μ_1 (64), μ_2 (50)		850	851	865	866	864	864
A'	827	818	818	t_1 (35), T^2 (12), θ (12), δ (13)		823	824	828	828	829	829
A''	805	802	808	μ_1 (30), Z(28), M(28)		808	808	811	811	811	810
A''	709	710		μ_1 (94)		712	713	721	716	720	719
A''	688	685		Z(96), μ_3 (30)		688		692	693	692	~690
A'	669	672	676	Ω (46), θ (12), Z(11)		676	676	676	676	677	679
A'	620	612	620	Ω (66), φ (17)		617	619	618	618	619	620
A'	483	485	482	γ (40), Φ (19), θ (15)		482	483	483	481		509
A''	446			Z(108)			440	446	448	420	421
A'	409		410	Z(137)			406	408	410	409	410
A'	360	358	360	δ (35), I'(20), Ω (16)			360				364

^a From ref.⁸.

TABLE II

Interpretation of infrared and Raman spectra of dimethyl terephthalate in the range 1750—140 cm^{-1} . PED designates "potential energy distribution"; ρ depolarization factor. Wavenumbers which can be assigned to more than one vibrational mode are given in parentheses

Symmetry	Calculation ^a	IR		RA		PED		Melt		Crystal	
		ν, cm^{-1}		ν, cm^{-1}				IR	RA	IR	RA
A_g	1 723		1 728	S(90)							
B_u	1 721	1 724		S(93)			1 730	1 731		1 724	
A_g	1 606		1 616	T(74), ρ (25)				1 612		1 722	
A_g	1 576		1 580	T(82), ρ (13)			1 577 ^b	1 577		1 609	
B_u	1 504	1 504		ρ (54), T(39)			1 505			1 576	
A_g	1 462		1 454	α (66), ψ (39)				~1 463		1 505 ^c	
B_u	1 461			α (67), ψ (39)			~1 463			1 449	
A_g	1 437		(1 436)	ψ (72), α (27)			(1 438)	1 436		1 449	
B_u	1 437	(1 434)		ψ (71), α (27)			(1 438)			1 439 ^d	
B_g	1 434		(1 436)	ψ (74), α (25)			(1 438)			1 443 ^d	
A_u	1 434	(1 434)		ψ (74), α (25)			(1 438)			1 434 ^{d,c}	
B_u	1 406	1 409		T(46), ρ (39)			1 410	1 409 ^b		1 428	
A_g	1 314		1 310	ρ (76)				1 306		1 409 ^c	
B_u	1 296	1 282		T(140)			(1 276)	1 282		1 282	
A_g	1 267		1 286	t_1 (35), θ (19), T'(41)			(1 276)	1 282		1 279	
B_u	1 250	1 262		t_1 (46), T'(38)			(1 276)			1 264	
A_g	1 185		1 195	α (43), ψ (17), ρ (17)			1 193			1 205	
B_u	1 181	1 195		α (55), ψ (20)						1 195	
A_g	1 176		1 179	ρ (55), T(14), α (14)			(1 178 ^b)	1 174		1 174	
B_g	1 158		1 158	α (71), ψ (26)						1 169	
A_u	1 158			α (71), ψ (26)			(1 178)			1 167	
B_u	1 109	1 115		ρ (27), ρ (19), T(13), t_1 (14)			1 116	1 113 ^b		1 116	
B_u	1 101	1 108		ρ (46), T(30)			1 105			1 108	

	1 092	1 018	1 107	T(35), τ_1 (26), τ_2 (13) Ω (38), φ (27), T(28)	1 021	1 103	~0.1	1 019 1 014 984	1 106 ^c
A_g	1 019								
B_u									
A_u	991			μ_2 (125)					980
B_g	972			μ_2 (136)					959
A_g	956	963	963	τ_2 (85)	(965 ^b)	960	0.3	956	
B_u	955	952	952	τ_2 (90)	(965)			879	
A_u	870	878	878	μ_2 (88)	874			874	
B_g	859			μ_2 (124)					859
A_g	838		848	τ_1 (30), T(20), δ (12)	837 ^b	836	0.06		841
B_u	819	817	817	τ_1 (39), δ (15), θ (13)	812	812 ^b	0.5	817	
B_g	802		804	Z(45), M(39), μ_3 (49)	796 ^b	794	0.74		800
A_u	729	730	730	μ_3 (59), μ_2 (46)	731	730 ^b	0.5	737	796
A_g	701		709	Ω (36), T'(16), θ (17)	706 ^b	704	0.03		705
B_g	675		623	Z(88), μ_2 (36)					682
A_g	629			Ω (63), φ (16)	633 ^b	632	0.74	633	
A_g	513		519	Φ (34), γ (34)	529				503
B_u	495	500		θ (34), T'(32)	499			498	
A_u	472	475		Z(89), M(80)				475	
B_u	436	438		γ (36), δ (26)	432			466	
A_u	411			Z(135)				433	
A_g	344		355	δ (65), θ (23)	350 ^b	348	0.19	409	351
B_u	323	324		δ (51), γ (14), θ (19)	322	327 ^b	0.2		
A_g	264		273	T'(22), Ω (22), θ (13), Φ (12)		274	0.57	323	288
B_g	252			M(64), τ_3 (20)		265	0.19		269
A_u	215			τ_3 (96)		258 ^b	0.12		
B_g	207	195	195	τ_3 (77), M(15)		(178)	0.75		191
A_g	165	144	144	γ (54), Φ (39)		(178)			143

^a From ref. ^{8, b} Bands corresponding to the form with the mutual *cis* orientation of the two ester groups; ^c bands exhibiting splitting at temperatures below -100°C; ^d bands appearing in the spectrum at temperatures below -100°C.

two ester groups on the aromatic ring. For these conformers, the mutual positions of near atoms are equal, and the conformers differ only by symmetry (*IIIa,b* in Scheme 1). As in the solid state, dimethyl terephthalate has a planar structure with a mutual *trans* orientation of ester groups, the infrared bands at 1577, (1178), 965, 837, 796, 706, 633 and 350 cm^{-1} and the Raman bands at 1409, (1178), 1113, 812, 730 and 327 cm^{-1} may be assigned as the bands of the conformer with the *cis* mutual orientation of the two ester groups (*IIIb*). The intensities of these bands in the spectra of liquid samples indicate that the populations of the conformers *IIIa* and *IIIb* are comparable; this is in agreement with the results of the measurements of dipole moments¹⁵.

The remaining conformationally sensitive band at 529 cm^{-1} can be observed only in infrared spectra of liquid samples (Fig. 5a). As in methyl benzoate a band sensitive probably to rotation about the CO—OCH₃ bond appears at 510 cm^{-1} , it is possible that a similar isomerism is also operative in dimethyl terephthalate. So far, this interpretation is not quite safe. For its verification, analysis of further model molecules will be required and will be the subject of our further studies.

Similarly as in methyl benzoate, also in infrared and Raman spectra of dimethyl terephthalate, a narrowing and splitting of bands of the methyl group is observed at temperatures far below the melting point, mainly in the range 1400–1500 cm^{-1} .

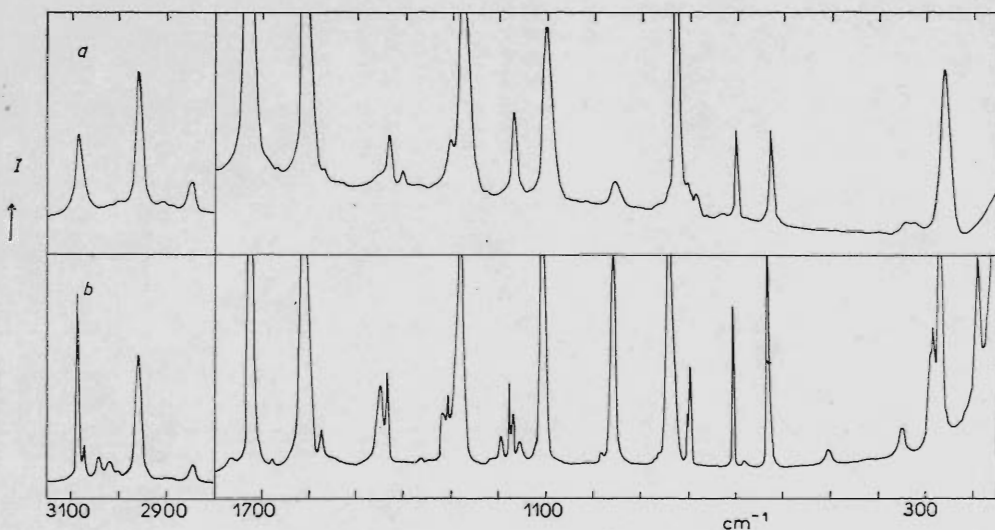


FIG. 6

Raman spectra of dimethyl terephthalate: *a* melt, *b* crystal

This splitting evidently is not connected with conformational structure and is probably due to intermolecular interactions.

In the spectra of dimethyl terephthalate measured by us we have detected some bands which have not been interpreted previously, and we have determined the bands which are characteristic of the *cis* form in the melt. By comparison of the wave-numbers of the vibrations of this ester in the crystalline and liquid states with the values calculated by Boerio and Bahl⁸, we were able to refine the interpretation of the vibrational spectra of crystalline dimethyl terephthalate, and to present an interpretation of the vibrational spectra of its melt which is summarized in Table II.

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