CONFORMATIONAL STRUCTURE OF ETHYLENE GLYCOL DIBENZOATE. VIBRATIONAL AND NMR SPECTRA

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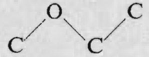
Received July 15th, 1980

It was found that three crystalline forms of ethylene glycol dibenzoate can be prepared. Infrared and Raman spectra of these three forms, as well as of the glassy and liquid states, were measured. From $^3J_{HH}$ coupling constants obtained by analysis of the ^{13}C satellite band of the $—CH_2—$ group in ^1H-NMR spectra, and from the $^3J_{CH}$ coupling constants of the $—CO.O.CH_2—$ fragment obtained by analysis of the carbonyl band in ^{13}C-NMR spectra it was found that in the liquid state the $—CH_2—CH_2—$ group exists predominantly in the gauche conformational structure, and the bonds  assume predominantly a *trans* orientation. The results of the analysis of NMR and vibrational spectra were used for the structural interpretation of conformationally sensitive bands in vibrational spectra of ethylene glycol dibenzoate.

Because of the presence of several single bonds in the molecule of ethylene glycol dibenzoate, a large number of rotational isomers may be expected to appear in this molecule. From X-ray diffraction it is known that in a monocrystal prepared by crystallization from a mixture of methanol and acetone[1] (crystalline form A), ethylene glycol dibenzoate has a planar structure with a *trans* conformation of the ethylene glycol fragment (Fig. 1*a*). From measurements of infrared spectra it is known[2-4] that slow cooling of an ethylene glycol dibenzoate melt yields a second crystalline modification which in this paper will be designated as the crystalline form B, and that in the liquid state this compound is also present in a different conformational form than that found by X-ray analysis of the crystalline form A. A comparison of the infrared spectra of liquid ethylene glycol dibenzoate with the infrared spectra of ethylene glycol derivatives of known conformational structure indicated[3] that liquid ethylene glycol dibenzoate contains conformational forms with a *gauche* structure of the ethylene glycol fragment (Fig. 1*b*). Raman spectra have been measured only with the crystalline form A and have been used, together with the infrared spectra of this form, for the interpretation of the vibrational spectra of the planar structure of ethylene glycol dibenzoate based on force field calculations[5]. NMR spectra have not been used in studies of the conformational forms of ethylene glycol dibenzoate so far.

As ethylene glycol dibenzoate is an important model in studies of the conformational forms and vibrational spectra of poly(ethylene terephthalate), we have attempted to refine the data concerning the conformational structure and conformationally sensitive bands in vibrational spectra of this model compound. Therefore we have measured the infrared and Raman spectra of ethylene glycol dibenzoate in the crystalline states, in the glassy state and in the liquid, and we have attempted to present a structural interpretation of these spectra by comparison with the results of the analysis of ^1H and ^{13}C—NMR spectra of liquid samples.

EXPERIMENTAL

Preparation of ethylene glycol dibenzoate. The title compound was prepared by reaction of benzoyl chloride with ethylene glycol in the presence of dry pyridine. Both reaction components were previously purified by vacuum rectification. The reaction product was poured into dilute H_2SO_4 (*c*. 50% by vol.), from which crystals of ethylene glycol dibenzoate precipitated. These were further purified by recrystallization from ethanol. The chemical structure of the samples was verified by ^1H-NMR spectra, and the purity was determined from the melting endotherm using the Perkin–Elmer DSC-2 calorimeter and the procedure of Plato and Glasgow. For a 1 mg sample the purity found was 99·6%. Determination of the basic crystallographic parameters by X-ray diffraction confirmed that the crystalline structure of the monocrystals obtained from ethanol is identical with the structure described in the literature[1].

NMR *spectra.* ^1H-NMR spectra were measured by the FT-NMR technique at 200 MHz using the pulse spectrometer Varian XL-200. For the measurement of the ^{13}C satellite bands in ^1H-NMR spectra, 200—300 transients were accumulated with a digital resolution of 0·1 Hz; because of the high dynamic range of this experiment, use was made of the double-precision routine with floating-point mathematics. ^{13}C-NMR spectra were measured on the spectrometer FX-60 (JEOL) at 15 MHz. In experiments with selective heteronuclear decoupling, the effect of the irradiating field was corrected similarly as in our previous communication[6].

Infrared spectra. Infrared spectra were measured on the spectrometers PE-621 and 580B. Spectra above room temperature were measured in a commercial Perkin–Elmer cell. Below room temperature the spectra were measured in a cell of our own construction[7].

Raman spectra. Raman spectra were measured on the Coderg LRDH-800 spectrometer. The spectra were excited by the line 514·5 nm of the argon ion laser CR-3 (Coherent Radiation).

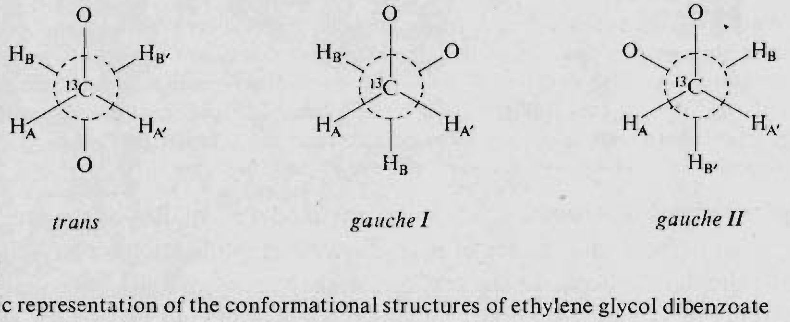
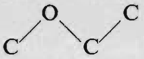


FIG. 1

Schematic representation of the conformational structures of ethylene glycol dibenzoate

The samples were measured in capillary cells in the 90° arrangement. The temperature dependence of Raman spectra was measured in a cell of Harney–Miller[8] type, and in a heated cell of our own construction[7].

Possible Conformational Forms of Ethylene Glycol Dibenzoate

In the present study, three types of conformational structures of ethylene glycol dibenzoate will be considered. First of these will be the conformers generated by rotation about the CH_2—CH_2 bond, of which the forms with an approximately *trans* structure of the ethylene glycol fragment (Fig. 1*a*) will be designated as *T*, and the forms differing from the former by rotation about the CH_2-CH_2 bond by an angle approximately equal to 120° will be designated as *G* (Fig. 1*a*). The second type of conformational structures is generated by rotation about the O—CH_2 bond. The structure with the *trans* orientation of the  bonds will be designated as *t* (Fig. 1*a*). The forms differing from the former by rotation about the O—CH_2 bond by an angle of 90°–120° will be designated as *g* (Fig. 1*c*). In our studies of ethyl benzoate[6] and methyl benzoate[9] it was found that besides the planar structures of the benzyl ester group, nonplanar structures may also occur. Analogous conformational structures in ethylene glycol dibenzoate will be designated as *v* (planar) and *w* (nonplanar). The forms *G*, *g*, *w* can be generated both by right-handed and by left-handed rotations from the forms *T*, *t* and *v*, respectively.

RESULTS AND DISCUSSION

NMR *Spectra*

a) Isomers generated by rotation about the CH_2—CH_2 *bond*. The conformational structure connected with the rotation about the ethylene C—C bond of ethylene glycol dibenzoate in C_6D_6 solution was determined from the values of $^3J_{HH}$ coupling constants obtained by analysis of ^{13}C satellite bands of CH_2 groups in ^1H-NMR spectra.

^{13}C satellite bands of the $OCH_2.CH_2O$ fragment (Fig. 2) correspond to transitions on the nuclei AA′ of the system AA′BB′X, where AA′ and X are the protons and the carbon of the group $^{13}CH_2$, BB′ are the protons of the group $^{12}CH_2$ neighbouring with ^{13}C. Each of the satellites can be also described as transitions on the *aa′* nuclei in two *aa′bb′* subspectra characterized by the effective frequencies $\nu_a = \nu_A \pm \frac{1}{2}J_{AX}$ and $\nu_b = \nu_B \pm \frac{1}{2}J_{BX}$, where the value of $J_{AX} = {}^1J_{CH}$ can be determined from the separation of the two satellites; the value $J_{BX} = {}^2J_{CH}$ can be set equal to zero in the analysis of the *aa′* transitions. Using the notation of Pople and coworkers[10], the structure of the satellite band is characterized by the constants $K = J_{AA'} + J_{BB'}$, $L = J_{AB} - J_{A'B} = J - J'$, $N = J_{AB} + J_{AB'} = J + J'$, $M = J_{AA'} - J_{BB'}$. As indicated in Fig. 2, approximate values of the parameters N and L can be directly determined from the spectra provided the resolution of the spectra is good enough. Because of partial band overlap and for improvement of accuracy, in our measurements the values of the parameters N and L were determined by comparison with the simulated *aa'bb'* subspectra. In this simulation the value of $J_{AA}' = J_{BB}'$ was set equal to -13 Hz (the shape of the spectra in our case is not sensitive to the value of this parameter, so that a rough estimate is sufficient). The obtained values of N and L which were found equal for both measured concentrations (50 and 80% ethylene glycol dibenzoate in C_6D_6), are given in Table I.

The relation between the coupling constants J and J', or the parameters N and L and the conformational structure of the fragment $OCH_2.CH_2O$, with the assumption of the presence of one T and two mirror-image G conformers (Fig. 3), was analyzed in detail in the paper by Matsuzaki and Ito[11]. By a complicated analytical procedure based on the assumption that the values of J_T and J_G are different in various conformers, these authors derived values of J_T, J_G which differ considerably from conventional ones. For this reason in this paper we have preferred a simpler procedure where we have approximated the values J_T and J_G by the same numbers in various conformers. Further we have assumed that the ratio $J_T : J_G = A$ lies within the limits 4–5 (ref.[12]). Then the constants J and J' are given by the relations (Fig. 3)

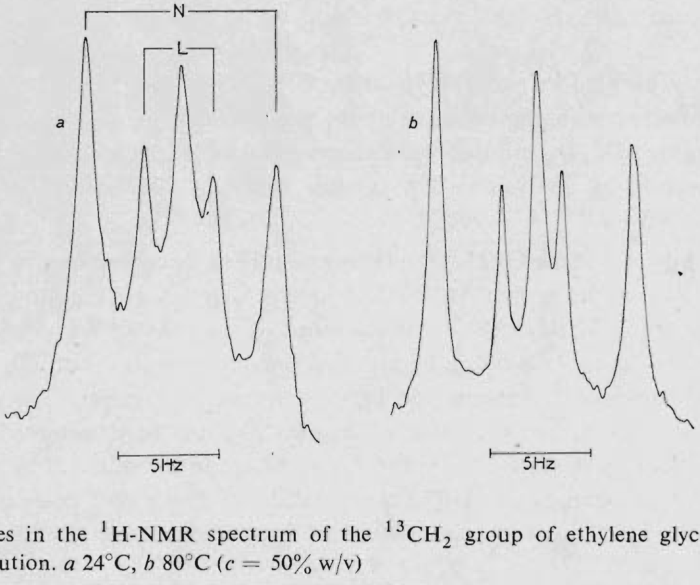


FIG. 2

^{13}C satellites in the ^1H-NMR spectrum of the $^{13}CH_2$ group of ethylene glycol dibenzoate in C_6D_6 solution. *a* 24°C, *b* 80°C (c = 50% w/v)

$J = J_{AB} = J_{A'B'} = n_T J_G + \frac{1}{2} n_G (J_T + J_G), J' = J_{A'B} = J_{AB'} = n_T J_T + n_G J_G$, where n_T and n_G are the populations of the conformers T and G, $n_G = n_{G_1} + n_{G_2}$ and $n_T + n_G = 1$. Simple algebra yields

TABLE I

NMR parameters and the population of the *trans* form n_T on the ethylene bond of ethylene glycol dibenzoate (50 and 80% in C_6H_6)

t °C	A	N	L	J_G	J_T	n_T
25	4	9·5	3·4	2·66	10·63	0·049
	5			2·28	11·39	0·085
61	4	9·75	3·20	2·70	10·82	0·070
	5			2·32	11·59	0·100
82	4	9·9	3·0	2·72	10·90	0·089
	5			2·34	11·68	0·119

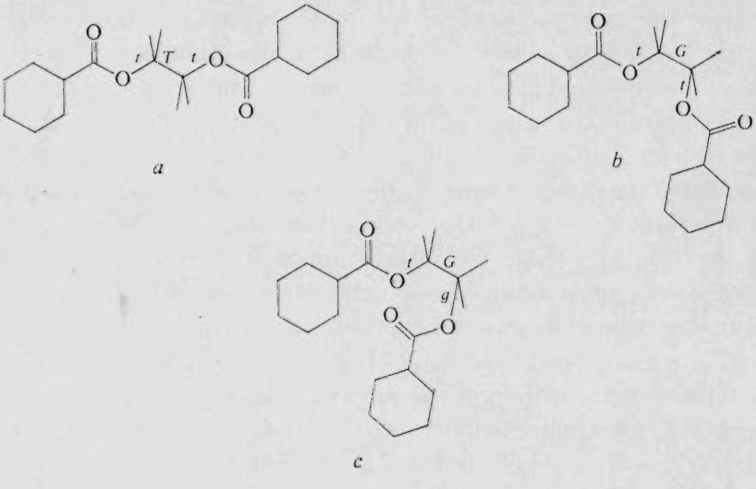


FIG. 3

Schematic representation of the conformational forms generated by rotation about the CH_2—CH_2 bond of ethylene glycol dibenzoate

$$N = \tfrac{1}{2}(A + 3)\,J_G + \tfrac{1}{2}(A - 1)\,n_T J_G\,, \quad L = \tfrac{1}{2}(A - 1)\,J_G - \tfrac{3}{2}(A - 1)\,n_T J_G\,,$$

$$J_G = (3N + L)/(2A + 4)$$

$$n_T = (N - \tfrac{1}{2}(A + 3)\,J_G)/(\tfrac{1}{2}(A - 1)\,J_G) = (-L + \tfrac{1}{2}(A - 1)\,J_G)/(\tfrac{3}{2}(A - 1)\,J_G)\,.$$

The values of J_G and n_T calculated by this procedure for the temperature range 25–82°C are given in Table 1. The obtained values of J_G and the corresponding values of J_T are within the conventional limits both for $A = 4$, and for $A = 5$; also the temperature dependence of J_G is negligible and evidently within the limit of experimental error. The absolute value and the temperature dependence of n_T for $A = 5$ conforms very well to the free energy difference $\Delta G = 4{\cdot}2$ kJ/mol.; for $A = 4$ the absolute values of n_T would indicate a $\Delta G = 5{\cdot}0-5{\cdot}5$ kJ/mol, however their temperature difference is steeper than expected for this value of ΔG. For this reason, the values calculated with $A = J_T : J_G = 5$ are preferred.

To summarize: measurements of ^{13}C satellites in ^1H-NMR spectra indicate that in solution the conformation on the ethylene bond of ethylene glycol dibenzoate is predominantly *G*, with less than 10% of the *T* form at room and moderately elevated temperatures, and ΔG between the *T* and *G* forms is $\sim 4{\cdot}2$ kJ/mol.

b) *Isomers generated by rotation about the* $O—CH_2$ *bond.* The conformational structure generated by rotation about the $O—CH_2$ bond was approximately determined by a procedure similar to that used in the preceding paper[6] for ethyl benzoate, from the coupling constant $^3J_{CH}$ of the fragment $—CO.O.CH_2—$, obtained by analysis of the carbonyl band in ^{13}C-NMR spectra, measured with selective heteronuclear decoupling of aromatic protons in the *o*-position. The experimental conditions of these measurements were the same as in the preceding paper[6] for ethyl benzoate, and also the correction of the effect of the irradiating field was calculated in the same manner.

The structure of the carbonyl band of ethylene glycol dibenzoate corresponds to the X band of the system XAA'A''A'''. Therefore the band shape should be roughly a quintet with a spacing of $1/2J_{AX}$. The experimental shape of the carbonyl band which exhibits only indications of fine structure corresponds to this assumption. Therefore we have attempted to determine the value of $^3J_{CH}$ from a comparison of the width and shape of this band with a simulated band shape. The interproton coupling constants needed for this simulation were taken from the previously described analysis of ^{13}C satellites in the ^1H-NMR spectrum of the $—OCH_2.CH_2O—$ fragment ($J_{AA'} = J_{A''A'''} = -13$ Hz, $J_{AA''} = J_{A'A'''} = (1/2)(N + L) = 6{\cdot}45$ Hz, $J_{AA'''} = J_{A'A''} = (1/2)(N - L) = 3{\cdot}05$ Hz). The experimentally determined width at half height (3·3 Hz) and a corresponding shape of the carbonyl band can be achieved with a value of $J_{AX} = J_{A'X} = 2{\cdot}2$ Hz, with a convolution of the stick spectrum by a Lorentzian shape of width at half height $\Delta\nu_{1/2} = 1{\cdot}35$ Hz. The shape of the carbonyl band could also be matched by using a smaller J_{AX} and larger $\Delta\nu_{1/2}$, but even $\Delta\nu_{1/2} = 1{\cdot}35$ Hz is already larger than was customary in analogous measurements of ethyl benzoate and methyl benzoate, and it is very improbable that the real $\Delta\nu_{1/2}$ could be even larger. Larger values of J_{AX} with smaller $\Delta\nu_{1/2}$ lead to a more pronounced fine structure of the carbonyl band and are therefore excluded. Therefore we consider the value of $J_{AX} = 2{\cdot}2$ Hz as sufficiently determined. After correcting for irradiation, the experimental value $J_{AX} = 2{\cdot}2$ Hz leads to $^3J_{CH} = 2{\cdot}57$ Hz. This value is lower than the corresponding value for ethyl benzoate. Assuming the presence of a single conformer and using the simplest relation (*1*) from ref.[6], this result indicates a structure with the CH bonds of the CH_2 group forming the angles 82° and 38° with the plane of the ester group, *i.e.* a structure with the CH_2—CH_2 bond twisted 22° out of this plane; this structure is nearer to a fully planar structure than was found for ethyl benzoate. Assuming the presence of two forms, *t* and *g* (twisted 120° out of the plane), the value of $^3J_{CH}$ corresponds to the population $p_t = 0{\cdot}8$, both using relation (*1*) or (*2*) of ref.[6]. Assuming the pressence of the form *t* together with the form *g* twisted 90° out of the plane, relation (*1*) of ref.[6] yields $p_t = 0{\cdot}86$, relation (*2*) of ref.[6] yields $p_t = 0{\cdot}81$. In the following we shall consider $p_t = 0{\cdot}83 \pm 0{\cdot}03$.

The analysis of ^{13}C-NMR spectra therefore indicates that in ethylene glycol dibenzoate, the *t* conformation on the O—CH_2 bond predominates even more strongly than in ethyl benzoate. The combined results of the analysis of ^{1}H and ^{13}C-NMR spectra indicate that for a solution of ethylene glycol dibenzoate in C_6D_6, the population of the *G* structure of the ethylene fragment $p_G = 0{\cdot}915$, and of the *T* structure $p_T = 0{\cdot}085$. Rotation about the O—CH_2 bond yields *t* structures with a population $p_t = 0{\cdot}83 \pm 0{\cdot}03$, and *g* structures with a population $p_g = 0{\cdot}17 \pm 0{\cdot}03$. From these values it can be calculated that at room temperature in the solution of ethylene glycol dibenzoate, 68–60% of the molecules have the structure *tGt*, 22–28% the structure *tGg*. The populations of the structures *tTt*, *gGg* and *tTg* amount to several per cent each, and the population of the structure *gTg* is negligible.

Raman Spectra

The Raman spectra of the crystalline forms A and B of ethylene glycol dibenzoate, prepared directly in the cells for the measurement of Raman spectra, are shown in Figs 4*a* and 4*b*. In Figs 4*c* and 4*d* are shown the Raman spectra of the melt and of the glassy state which was prepared by quenching in liquid nitrogen. While preparing the glassy state we have found that it is possible to prepare a further crystalline form which we designate as the crystalline form C. This crystalline form is stable only at very low temperatures, and at temperatures above −15°C it is transformed to the crystalline forms A or B, the contents of which differs according to the procedure. The corresponding Raman spectrum, with well pronounced sharp bands of the lattice vibrations characteristic of this crystalline state, is shown in Fig. 4*e*.

The Raman spectrum of the crystalline form A (Fig. 4*a*) differs considerably from the Raman spectra of liquid or glassy ethylene glycol dibenzoate as shown in Figs 4*c* and 4*d*. This is in agreement with the results of X-ray analysis of the crystalline form A and NMR analysis of ethylene glycol dibenzoate in solution, according to which the structure *tTt* of the crystalline form A is very poorly populated in the liquid state (less than 10%). The Raman spectra of the crystalline forms A and B differ only by small shifts of the wavenumbers of some bands, and by band intensity changes in the range 1 400 – 1 500 cm^{-1}. The most pronounced difference is observed in the range 800 – 815 cm^{-1} where form B exhibits a singlet at 802 cm^{-1} and form A a doublet at 803 and 811 cm^{-1}, and in the shape of the stretching vibration of the C=O bond. However, the carbonyl band is considerably affected by intermolecular

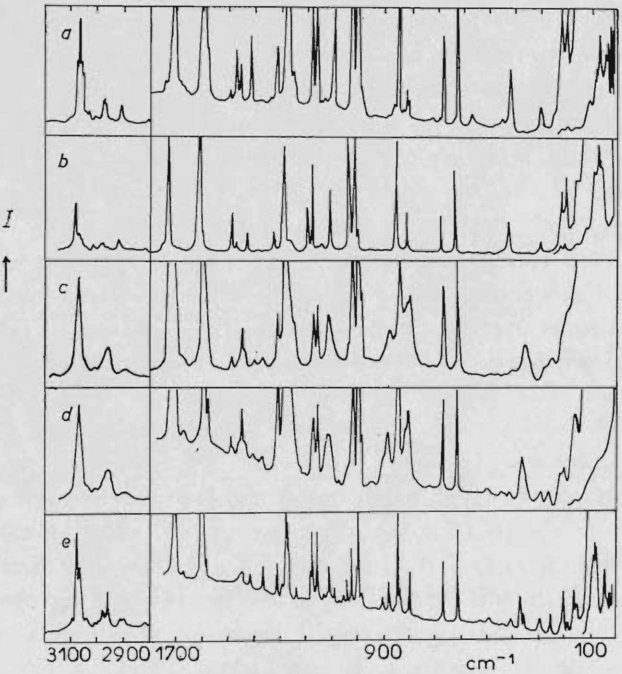


Fig. 4

Raman spectra of ethylene glycol dibenzoate. *a* crystalline form A, *b* crystalline form B, *c* melt, *d* glassy state, *e* crystalline form C interactions. In the melt this band is broad and asymmetrical; this asymmetry disappears in dilute CCl_4 solution, and it is also reduced in spectra measured at elevated temperature. The small differences between the Raman spectra of the crystalline forms A and B indicate that in these crystalline forms the molecules of ethylene glycol dibenzoate probably have the same conformational structure and that the crystals only differ by the mutual arrangement of the molecules.

The Raman spectra of the crystalline forms C, of the melt and of the glassy state (Fig. 4*c*, 4*d*, 4*e*) differ very little in band positions and intensities. Marked differences are observed only in the range below 600 cm^1, where the crystalline form exhibits bands of skeletal bending and lattice vibrations, which in the liquid state are either less conspicuous, or are completely missing. In the other ranges the only observed differences are the following: the crystalline sample exhibits bands at 1 044 and 1 058 cm^{-1} which are very inconspicuous in the melt and in the glassy state; the band at 813 cm^{-1} which is relatively strong in the melt and in the glassy state, is missing in the spectrum of the crystalline form C. Differences in band intensities are observed in the range 1 400 – 1 500 cm^{-1} which is evidently sensitive to the mutual arrangement of the molecules, as was already mentioned in the discussion of the spectra of the crystalline form A and B. The relation between the Raman spectra of the crystalline form C and of the melt and glassy state can be well explained if we assume that in the crystalline form C the molecule of ethylene glycol dibenzoate assumes the *tGt* structure. The overall agreement between the Raman spectra of the crystalline state C and of the liquid state is evidently due to the fact that in all these cases the molecule occurs in the *G* structure. The band at 813 cm^{-1} which is relatively strong in the spectrum of the liquid and which disappears in the spectrum of the crystalline form C can be assigned to the *gG* structure. This structure is relatively abundant in the liquid state and is not present in the crystalline forms. The bands at 1 047 and 1 058 cm^{-1} which are poorly defined in the spectra of the liquid and glassy samples and which are conspicuous in the spectrum of the crystalline form C, can be assigned to the *tGt* structure; in the crystalline form C this is the only conformer present and therefore it gives a well defined spectrum. The proposed structural interpretation of these bands is in agreement with the Raman spectra of ethyl benzoate[6] where the bands in the range about 800 cm^{-1} are sensitive to $t-g$ isomerism. The changes of band intensities in the range 1 400 – 1 500 cm^{-1} appearing upon transition from the liquid to the crystalline state C can be interpreted both by the sensitivity of these bands to the mutual arrangement of molecules, and by the $t-g$ conformational changes.

In the ranges about 500 and 250 cm^{-1} where methyl benzoate[9] and ethyl benzoate[6] exhibited Raman bands sensitive to *v* and *w* structures, also the spectra of liquid and crystalline ethylene glycol dibenzoate exhibit changes which indicate that also in this compound, the *w* structure of the benzyl ester group can be found. However, the interpretation of these changes is not unequivocal.

TABLE II

Interpretation of vibrational spectra of ethylene glycol dibenzoate. PED designates potential energy distribution, ϱ — depolarization factor in Raman spectra

Crystal A IR	Crystal A RA	Crystal B IR	Crystal B RA	Crystal C IR	Crystal C RA	Melt IR	Melt RA	ϱ	Structure sensitive bands	Symmetry	Calc.[5]	Assignment of bands for crystal in form tTt PED
ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}					ν, cm^{-1}	
	2 979		2 981		2 982		2 980^a		tTt	B_g	2 967	$R_2(99)$
2 980	2 972	2 979	2 971	2 975	2 976	2 980^a			tTt	A_u	2 957	$R_2(99)$
				2 960	2 959	2 960	2 959	~0·1	G			
	2 913		2 913		2 910		2 910^a	~0·6	tTt	A_g	2 889	$R_2(99)$
2 912		2 912		2 912		2 908^a			tTt	B_u	2 882	$R_2(100)$
				2 894	2 897	2 892	2 894	~0·1	G			
					1 716							
	1 718				1 710							
	1 713		1 721		1 706		1 723	0·14		A_g	1 722	$S(91)$
1 729												
1 712		1 719		1 716		1 726				B_u	1 722	$S(91)$
	1 603		1 606		1 605		1 601	0·50		A_g	1 598	$T(76)$, $\phi(26)$
1 602		1 604		1 603						B_u	1 598	$T(76)$, $\phi(26)$
	1 586		1 589		1 588		1 585^a	~0·7		A_g	1 586	$T(78)$, $\phi(23)$
1 585		1 585		1 585		1 585				B_u	1 586	$T(78)$, $\phi(23)$
	1 496		1 498		1 496		1 492	0·26		A_g	1 486	$\phi(59)$, $T(38)$
1 495		1 494		1 492		1 493				B_u	1 486	$\phi(59)$, $T(38)$
1 482		1 486		1 485^a		1 478^a			tTt	B_u	1 465	$\psi'(61)$, $\alpha'(35)$
	1 473		1 476		1 475		—	—	tTt	A_g	1 453	$\psi(52)$, $\alpha(40)$
	—		—	1 461	1 463	1 462^a	—	—	G^c			
	—		—	1 439^a	—	1 438	1 440	0·7	G^d			
1 453		1 454		1 453		1 453				B_u	1 449	$\phi(53)$, $T(39)$
					1 453							
	1 454		1 456		1 450		1 452	0·42		A_g	1 448	$\phi(49)$, $T(36)$

	1 418		1 418		1 420				$tTt + G^c$	A_g	1 395	$\beta(62)$, $\alpha'(27)$
					1 416							
	—		—		—		1 404	0·27	G^d			
—		—		1 399^a		1 399			G^d			
				1 373	1 372	1 370	1 370	0·7	G			
1 341		1 340		1 342		1 339			tTt	B_u	1 337	$\beta(46)$, $\alpha'(34)$
	1 317		1 318		1 320		1 315	0·14		A_g	1 325	$\phi(88)$
					1 317							
1 316		1 315		1 316		1 316				B_u	1 322	$\phi(74)$
				1 293	1 293		—		G^c			
	1 279^b		1 279^a		1 280	1 285^b	1 280^b	0·11		A_g	1 293	$T(129)$
			1 273^b		1 273^b							
1 272		1 271		1 282		1 285^b				B_u	1 291	$T(132)$
				1 269								
	1 279^b		1 279^a		1 280		1 280^b	0·11		B_g	1 285	$\beta(48)$, $\alpha'(62)$
			1 273^b		1 273^b							
1 258^b		1 259^b		1 263^b		1 265^b				A_u	1 271	$\alpha(94)$, $\beta(11)$
	1 254		1 254		1 247		1 260	0·3		A_g	1 265	$t_1(38)$, $T(36)$, $\Theta(20)$
					1 243							
1 258^b		1 259^b		1 263^b		1 265^b						
1 242		1 243^a				1 248				B_u	1 262	$t_1(45)$, $T(39)$, $\Theta(22)$
	1 184^b		1 185^b		1 186^b				tTt	B_g	1 174	$\beta(43)$, $\alpha'(39)$
	1 184^b		1 185^b		1 186		1 177^b	0·15		A_g	1 173	$\phi(73)$, $T(15)$
					1 180^b							
					1 180^b							
					1 170		1 177^b	0·15	G			
					1 180							
1 184		1 182		1 177	1 170^b	1 178	1 177^b			B_u	1 173	$\phi(73)$, $T(15)$
	1 166		1 165		1 160		1 159	0·67		A_g	1 159	$\phi(73)$, $T(25)$
					1 158							
1 162		1 159		1 159		1 160				B_u	1 159	$\phi(73)$, $T(25)$
	1 128		1 129		1 133		1 132^a			A_g	1 120	$t_1(40)$, $r(22)$

TABLE II
(*Continued*)

Crystal A		Crystal B		Crystal C		Melt		ϱ	Structure sensitive bands	Symmetry	Calc.[5] ν, cm^{-1}	Assignment of bands for crystal in form *tTt* PED
IR	RA	IR	RA	IR	RA	IR	RA					
ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}						
1 120		1 120		1 114^b	1 118^a	1 112^b	1 114^b		*tTt*	B_u	1 112	$t_1(30)$, $T(23)$, $\Omega(14)$, $t_2(10)$
					1 113^b							
				1 114^b	1 118^a	1 112^b	1 114^b	0·06	*G*			
					1 113^b							
	1 099		1 096		1 097^a	1 097^b	1 095^a		*tTt*	A_g	1 100	$r(40)$, $T(13)$, $\delta(10)$, $\gamma'(11)$
						1 097^b			G^d			
1 076		1 072		1 073		1 070				B_u	1 073	$T(42)$, $\phi(42)$
1 071	1 075^a		1 073^a		1 073^a		1 070^a			A_g	1 072	$T(42)$, $\phi(42)$
				1 056	1 058	—			G^c			
				1 046	1 044	1 043	1 040^a		G^c			
	1 032				1 028							
	1 025		1 026		1 025		1 025	0·05		A_g	1 018	$T(39)$, $\phi(30)$, $\Omega(22)$
1 032												
1 025		1 025		1 027		1 027				B_u	1 018	$T(42)$, $\phi(42)$
	1 004		1 005		1 002		1 002	0·02		A_g	1 002	$t_2(74)$
1 004		1 004		1 003		1 003				B_u	1 001	$T(39)$, $\Omega(38)$
	989		990		988		988	0·05		A_g	1 000	$T(43)$, $\Omega(30)$
	—		—		—		—			B_g	990	$\mu_1(115)$
994^{a,b}		—		993^{a,b}		—				A_u	990	$\mu_1(115)$
	—		—		—		—			B_g	983	$\mu_2(70)$, $\mu_1(56)$
994^{a,b}				993^{a,b}		—				A_u	983	$\mu_2(70)$, $\mu_1(56)$
981		986		987		975			*tTt*	B_u	969	$t_2(84)$
				981								
	935		937		937		—			B_g	931	$\mu_2(86)$, $\mu_1(33)$
					930							

943		943^a		943								
932^a		932		936		937				A_u	931	$\mu_2(85)$, $\mu_1(33)$
				932								
				902	907	899			G			
					901							
				882	884	881	878	0·16	G			
					882							
859^b		857^b		859^b	856^b	$855^{a,b}$				B_u	871	$\Omega(46)$, $T(16)$
846		—		848		847				A_u	852	$\mu_1(64)$, $\mu_2(50)$
	863				856^b					B_g	851	$\mu_1(64)$, $\mu_2(50)$
859^b		857^b		859^b	856^b	$855^{a,b}$			tTt	A_u	841	$\beta(97)$
	844		844		848		842	0·07		A_g	831	$\mu_1(19)$, $\Theta(14)$, $T(17)$, $r(11)$
					840							
						816^a	813		G^d			
	811		802		808		803	0·2		B_g	802	$\mu_3(40)$, $Z(30)$, $M(29)$
	803				803							
806		802		804		804				A_u	799	$\mu(34)$, $\mu_1(30)$, $Z(30)$
	—		709		712^a		712^a	~0·3		B_g	708	$\mu_1(93)$
718		709		711		710				A_u	708	$\mu_1(92)$
708												
	684		—		680		—			B_g	688	$\mu_3(34)$, $Z(89)$
689		682		685		688				A_u	687	$Z(86)$, $\mu_3(35)$, $\mu_1(36)$
681												
673				674		676						
668						673				B_u	678	$\Omega(46)$, $T'(16)$
	672		674		671		672	0·05		A_g	664	$\Omega(46)$, $\Theta(16)$, $T'(12)$
617		617		618		618				B_u	621	$\Omega(66)$, $\phi(17)$
	618		619		614		616	0·75		A_g	620	$\Omega(64)$, $\phi(16)$
	559		559		556		550^a			A_g	539	$\gamma(44)$, $\Phi(12)$, $\gamma'(19)$
				522	522	529			G^f			
481		479		489	486	489	487^a		tTt^e	B_u	485	$\gamma(40)$, $\Phi(18)$, $\Theta(15)$
				463	458	463	465^a		G			

TABLE II

(*Continued*)

Crystal A IR	Crystal A RA	Crystal B IR	Crystal B RA	Crystal C IR	Crystal C RA	Melt IR	Melt RA	ϱ	Structure sensitive bands	Symmetry	Calc.[5] ν, cm^{-1}	Assignment of bands for crystal in form *tTt* PED
ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}		ν, cm^{-1}						
	444^b		$442^{a,b}$		439^b		430^b	0·67		B_g	448	$Z(106)$, $M(51)$
436^b		435^b		437^b		434^b				A_u	448	$Z(106)$, $M(51)$
405		399		404		401			*tTt*	B_u	427	$\delta(34)$, $\gamma'(26)$
	444^b		$442^{a,b}$		439^b		430^b			B_g	409	$Z(138)$
436^b		435^b		437^b		434^b				A_u	409	$Z(138)$
	408		408		406		407^a	~0·3	*tTt*	A_g	404	$T'(19)$, $\Theta(16)$, $\Omega(17)$, $\gamma'(11)$
					$\left\{\begin{array}{l}370\\358^b\end{array}\right.$		353^b	0·21	*G*			
353		350		356	358^b	350	353^b	0·21		B_u	344	$\Theta(21)$, $T'(17)$, $\Omega(16)$
						335	335^a		G^d			
	291		288		295	280	278	0·13	tTt^e	A_g	275	$\Phi(38)$, $\delta(24)$, $\Theta(19)$
					284							
							248	0·14	G^f			

[a] Poorly defined lines, [b] one experimental band can be assigned to several calculated bands, [c] band probably corresponds to conformational forms containing *tG* structures, [d] band probably corresponds to conformational forms containing *gG* structures, [e] band may correspond to structure *v*, [f] band may correspond to structure *w*.

By comparison of the Raman spectra of all the forms of ethylene glycol dibenzoate, and considering the above discussed structures of these forms, it may be decided which bands are common to all conformational forms, and which are characteristic of the *tTt*, *tGt* and *tGg* structures. This assignment is summarized in Table II.

Infrared Spectra

Infrared spectra of the crystalline forms A, B, of the melt and of the glassy state and of the crystalline form C are shown in Fig. 5*a* – *e*, respectively. Also in the cells for the measurement of infrared spectra we have never succeeded to prepare a completely pure crystalline form C. It always contained some amount of the crystalline forms A and B. This evidently depends on the method of preparation in consequence of the fact that already at temperatures about –50°C the crystalline form C is slowly transformed to the crystalline forms A and B. As seen from Figs 5*a* and 5*b*, the infrared spectra of the crystalline forms A and B are practically identical above 400 cm^{-1}. Differences are observed only in the shifts of some bands, which, however, are all less than 5 cm^{-1}; in intensity changes of some bands which may be observed *e.g.* in the range 1 380 to 1 500 cm^{-1}, and in the shape of the band of the carbonyl stretching vibration. All this is in agreement with the interpretation introduced in the chapter on Raman spectra, according to which the molecules of ethylene glycol dibenzoate have the same conformational structure *tTt* in both crystalline forms A and B.

Marked differences are observed between the infrared spectra of the crystalline forms A and B (Fig. 5*a*, 5*b*) on one hand, and the spectra of the liquid, of the melt and of the crystalline form C (Fig. 5*c*, 5*d*, 5*e*) on the other hand. These differences can be well explained by the interpretation introduced in the chapter on Raman spectra, namely that the liquid state is formed mainly by the *tGt* and *tGg* conformational structures and contains only a very small amount of the *tTt* structure, and that the crystalline form C is formed exclusively by the *tGt* conformer. By comparing the infrared spectra of all the forms of ethylene glycol dibenzoate it can be found which bands are characteristic of the *tTt* structure, which bands are common to all conformational structures, and which bands appear in forms with the *G* structure of the ethylene glycol fragment. This assignment is given in Table II. Our assignment of the bands characteristic of the *G* and of the *tTt* structures, and of the bands common for all the conformers is more complete and differs somewhat from the findings of ref.[4].

The preparation of the crystalline form C has made possible a more precise structural interpretation of some bands characteristic of the G conformational structures. Well pronounced bands in the spectra of the crystalline form C at 1 046, 1 056 cm^{-1} which are poorly defined in infrared spectra of the liquid and of the glassy state, are evidently bands of the *tGt* conformational structure. Bands at 1 399 and

1 097 cm^{-1} which are stronger in the spectra of the liquid and glassy state than in the spectra of the crystalline form C should be assigned to the *gG* conformational structures.

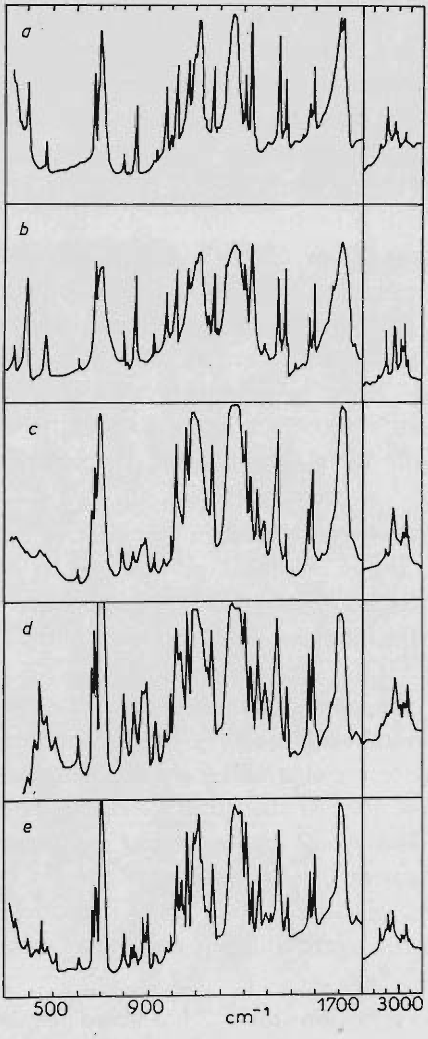


FIG. 5

Infrared spectra of ethylene glycol dibenzoate. *a* crystalline form A, *b* crystalline form B, *c* melt, *d* glassy state, *e* crystalline form C

Infrared spectra were also used for the determination of the enthalpy difference ΔH between the conformational structures T and G. For this we made use of the band characteristic of the T conformational structure at 1 339 cm^{-1} and of the band of the G conformational structure at 1 370 cm^{-1}. This pair was selected because the bands are well separated, their intensities in the liquid state are comparable and the bands do not differ much in frequency. The bands were measured in the temperature range 90–260°C, and the calculation of ΔH was based both on maximum absorbances, and on integrated band areas in absorbance scale. From absorbance maxima we found $\Delta H = 4{\cdot}2 \pm 0{\cdot}8$ kJ/mol, from the band areas $\Delta H = 3{\cdot}6 \pm 0{\cdot}6$ kJ/mol. These values are in very good agreement with the values found for the T and G isomers from NMR spectra.

Similarly as with methyl benzoate, ethyl benzoate, dimethyl terephthalate and diethyl terephthalate[6,9] we have tried to find bands characteristic of the v and w conformational structures. These might be the bands at 529 and 248 cm^{-1}. However, the dependence of these bands on the v and w structural changes is rather problematic and it cannot be safely determined to what extent v and w structures contribute to the observed change of these bands.

Our measurements have revealed some bands characteristic of the planar structure of ethylene glycol dibenzoate which have not been described previously. We have therefore made use of the calculated wavenumbers of bands in infrared and Raman spectra[5] for the interpretation of the spectra of the tTt conformational structure of ethylene glycol dibenzoate which is also given in Table II.

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Translated by D. Doskočilová.