Spectroscopic and conformational study of phenyl benzoate

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IR spectra of phenyl benzoate (PB) have been studied at various temperatures. On the basis of the calculation of the frequencies and forms of the normal phenyl benzoate molecule, the complete assignment of vibrational spectra was achieved. A conformational analysis of PB was carried out using molecular mechanics calculations. It was shown that the relative orientation of the benzene rings varies with temperature and phase state.

Key words: phenyl benzoate, conformation, IR spectrum, normal coordinate calculation.

The phenyl benzoate (PB) group is a fragment in a large number of low-molecular weight compounds and polymeric liquid crystals (LC) that are of great importance for theory and practice. The PB group can exist as several rotamers. Its conformational behavior is the governing factor in the existence of the LC phase.

An early study of the IR spectra of alkylenearomatic LC esters containing the PB fragment found some of the bands to be sensitive to temperature and phase changes.[1] It was possible to connect this observation with the conformational inhomogeneity of the fragment. At the same time the direct dependence of the vibrational frequencies of PB on changes in the angles of internal rotation remained obscure.

The study of the structure of molecules able to exist in the LC phase by vibrational spectroscopy calls for a detailed analysis of the dependence of the spectral characteristics on the conformation of the molecules. There has not yet been an analysis of this kind for PB. Early studies of the spectra of benzoates[2—5] appear to have been insufficient. According to Ref. 5, there are two most probable conformers of PB, one of which is totally planar, while the phenoxy group of the other is orthogonal to the plane of the ester group (EG). This inference is in conflict with the X-ray diffraction data[6] and with the results of quantum-chemical studies[7—10] as well. Hence, it requires verification.

The present work considers the structural peculiarities of PB in the condensed phase. For this purpose the frequencies and forms of the normal vibrations of PB were calculated, as was the conformation. The conformational study was based on the methods of molecular mechanics (MM). We compared the results obtained with the temperature and phase changes in the IR spectra. Additionally, we propose detailed assignments of the vibrational spectrum of PB.

Experimental

IR spectra of PB were recorded with Perkin Elmer 577 and Specord M80 IR spectrometers using a thermostatted cell. The temperature dependence of the spectral characteristics was determined in the interval between 10 and 72 °C. The sample temperature was lowered to the minimum value using two approaches: either by slow equilibrium cooling with increments of 1°, with samples kept at each temperature for 15 min, or by fast cooling over 30 min. The samples were prepared either as KBr pellets, 1% benzene solutions or capillary films between KBr disks.

Computation methods. The conformational analysis of the PB molecule was carried out by MM methods with due regard for π-conjugation. The MMX88 program set with standard parametrization was used on a PC AT-286. The optimization of the PB structure was performed in the context of the MM procedure. The energy and the structural parameters calculated were compared with those of the PB molecule in the conformation found by the X-ray crystallographic measurements. The potential curves for the rotations around the three internal axes were calculated. The strain energy was determined by varying each of three angles (τ_1, ϕ, τ_2) one after another from 0 to 180° with 30° increments. While one of the angles was being varied, the other two were free to change. While varying τ the calculation of each point was started with the plane of the benzene cycle (Ph^1) in line with the plane of the ester group (EG) and the plane of the Ph^2 cycle perpendicular to the rest of the molecule. This made it possible for the *cis*-conformation to occur in the initial position and for the maximum π-conjugation to occur between Ph^1 and the C=O group. The results are presented in Table 1.

The calculation of the frequencies and forms of the normal vibrations of the PB molecule was carried out in the manner of the calculation of the fragments using the program set from Ref. 11 adapted for a PC AT by O. V. Fateev (Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow). PB was built of fragments of toluene[12] and phenylacetate.[5] The structural parameters of the EG and the values of the torsion angles were taken from the X-ray diffraction data

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Table 1. The dependence of the strain energy E (kcal/mol) of phenylbenzoate on the internal rotation angles

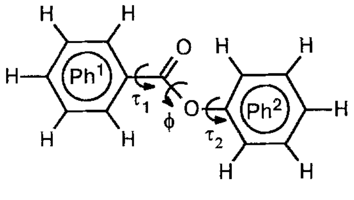
ϕ	τ_1	τ_2	E
0	−47.64	−53.70	35.70
30	33.29	33.09	36.00
60	17.64	11.63	38.09
90	4.99	5.98	38.49
120	−5.25	−1.99	37.04
150	−1.00	−22.52	34.30
180	8.68	−40.10	33.29
177.6	−7.52	−39.08	33.27*
−175.6	0	41.1	33.28
−175.9	30	42.5	33.25
−175.9	58	44.1	34.05
−175.2	89	42.80	34.44
−173.0	−29.52	0	34.02
−174.9	−9.96	30	33.58
174.3	1.55	60	33.57
179.2	3.16	89	34.14
178.8	3.52	120	33.58
171.4	2.13	150	33.33
164.65	12.87	179	34.14
179.85	−9.52	66.95	33.83**

* The stable structure of PB calculated by the MM method.
** The structure defined by the X-ray method.[5]

($\tau_1 = 10°$, $\tau_2 = 67°$).[6] The initial set of force constants[5,12] was refined through by varying them to give a satisfactory fit with the observed frequencies. To find the dependence between the vibrational frequencies and τ_1 and τ_2 with the resulting force field τ_1 and τ_2 were varied from 0 to 90°. The experimental and calculated frequencies and their assignments (in terms of the potential energy distribution) are given in Table 2.

Results and Discussion

The molecule of PB is composed of three planar fragments, namely, the EG and the two benzene rings. It has three axes of internal rotation. The rotations around the axes are given by three angles (τ_1, ϕ, τ_2):



The conformational analysis of the PB molecule gave the following results. The calculation of the potential of internal rotation as a function of the central torsion angle ϕ with free movement of τ_1 and τ_2 showed that for the PB molecule in the cis-conformation region, those conformers occur in which when ϕ decreases; the more flat the EG the more the angles of rotation of both benzene rings increase. In the region of the *trans*-conformations, due to π-conjugation the Ph^{1}COO fragment tends towards a planar configuration ($\tau_1 = 9°$) while the rotation angle of Ph^2 becomes significant ($\tau_2 = 40°$).

The barrier to internal rotation ($\Delta E^*(\phi)$) when going from the *trans*-form to the *cis*-form, was defined as 5.2 kcal/mol. The barrier to *cis—trans* isomerization is 2.75 kcal/mol. The difference in the energy (ΔE) between the two rotational forms is 2.45 kcal/mol in favor of the *trans*-form. The stable conformer of PB found by the MM method is a practically pure *trans*-form ($\phi = 178°$). The benzene rings are rotated $\tau_1 = -7.52°$ and $\tau_2 = 39.08°$. The calculated energy differs from the energy of the molecule with the crystal cell torsion angles ($\tau_1 = -10,°$ $\phi = 180°$, $\tau_2 = 67°$)[6] by a value less than kT (0.56 kcal/mol).

According to the MM method, the barriers to the rotation through τ_1 and τ_2 are 1.16 and 0.95 kcal/mol respectively (Table 1).

The results obtained may be correlated with the literature data in the following way. As in aliphatic esters (AE), the *trans*-configuration of PB ($\phi = 180°$) is more stable thermodynamically than the *cis*-form. The barrier $\Delta E^*(\phi)$ calculated by the MM method is close to the average of the experimental values (~6.4 kcal/mol) found in AE.[13a] The difference in energy between the *cis*- and the *trans*-forms correlates well with $\Delta H°$ of AE (~3.1 kcal/mol). The value of $\Delta E^*(\tau_1)$ seems to be low since the mean value of the experimental rotation barriers in benzaldehyde and acetophenone[13b] is 3.9 kcal/mol. Unfortunately there is no experimental $\Delta E^*(\tau_2)$ data for any molecules in the literature.

Using the neglect of differential overlap methods (NDO) led to the following results. Within the approximation of the NDDO:[7] $\tau_1 = 0°$, $\phi = 180°$ and $\tau_2 = 60°$; variations in τ_1 from -15 to $+15°$ practically do not change the energy of the molecule. In the context of the INDO method:[8] $\tau_1 = 50°$, $\phi = 0°$ and $\tau_2 = 40°$; $\tau_1 = 50°$, $\phi = 180°$ and $\tau_2 = 30$—$90°$ (gently sloping minimum); both the structures are equal in energy. The barrier to *cis-trans* isomerization $\Delta E^*(\phi)$ is 4.96 kcal/mol. The barrier to rotation of the phenyl rings ΔE^* is 4.6 kcal/mol. According to the CNDO method: for the same structural parameters[8] the *trans*-form is preferred to the *cis*-form by only 0.72 kcal/mol. Thus, the NDO methods which give different values of τ_1, correlate well as far as the values of the other angles are concerned. However, the *cis*- and the *trans*-conformations are practically degenerate.

The conformational analysis of the PB analog, 4-hydroxy-4'-carboxyphenylbenzoate, using the semiempirical method AM1 [10] gave the following angles: $\tau_1 = 0°$, $\phi = 180°$ and $\tau_2 = 45°$. Even when divided by the scale factor (1.9), the internal rotation barriers calculated were higher than those obtained before: $\Delta E^*(\tau_1) = 5.3$, $\Delta E^*(\phi) = 12$, and $\Delta E^*(\tau_2) = 2.12$ kcal/mol. Note that only the first value compares well with the experi-

Table 2. Experimental and calculated frequencies of vibrations of phenyl benzoate (ν/cm^{-1}). Potential energy distribution, PED(%)

Vibrational number	ν/cm^{-1}			Vibrational assignments	
	Experiment		Calculation		
	Crystal	Liquid		PED(%)	Ring
1—10	—	—	—	ν C—H	
11	1726 s	1735	1735	71, Q(C=O); 12, Q(C—O)	1,2
12	1615		1608	77, Q; 12, β	1
13	1593		1605	80, Q; 10, β	1,2
14	1589		1603	80, Q; 10, β	1,2
15	1582	1590	1599	78, Q; 12, β	2
16	1495 sh	1490 s	1496	32, Q; 61, β	2
17	1482 s	1485 sh	1494	31, Q; 62, β; 4, Q(C_{arom}—O)	1
18	1451 sh		1449	32, Q; 60, β	2
19	1449 s	1450 vs	1444	32, Q; 62, β	1
20	1318 m		1332	57, Q; 37, β	1
	1325 sh		1340	ν_{20} at $\tau_2 = 30°$	1
21	1312 m	1315 m	1331	44, Q; 50, β; 4 β_3	2
22			1303	78, Q; 21, β	2
23	1297 w	1295 sh	1301	68, Q; 31, β	1
24	1270 s	1265 vs	1253	11, Q; 39, Q(C_{arom}—O); 20;Q(CO)	1
25	1200 vs	1200 vs	1213	23, Q; 11, β; 49 Q(C_{arom}—O)	2
26	1180 m		1180	92, β	2
27	1170 m	1179 vs	1179	92, β	1
28	1160 m		1154	85, β	2
29	1155 m	1163 s.bd	1154	84, β	1
30	1084 s	1081 vs	1095	23, Q; 14, β; 34 Q(C_{arom}—O)	1,2
31	1070 s		1072	53, Q; 29, β; 4 Q(CO)	1,2
32	1065 s	1065 vs.bd	1063	57, Q; 24, β; 8, Q(CO)	1
33			1022	61, Q; 21, α; 17, β;	1
34	1025 s	1026 vs	1021	62, Q; 20, α; 6, β;	2
35			999	41, Q; 41, α; 10, β;	2
36	1004 vs	1002 vs	998	62, Q; 27, α; 7, β;	1
37			984	90, ρ; 10, χ	1
38	990 m	990 sh	981	92, ρ; 8, χ	2
39			965	95, ρ; 5, χ	2
40	979 m	980 sh	965	95, ρ; 5, χ	1
41	937 m	939 m	936	85, ρ; 10, χ; 3, ρ(C=O)	1
42	922 s	915 s	915	75, ρ; 8, χ; 6, Q(C_{arom}—O)	2
	919 s		909	ν_{42} at $\tau_2 = 30°$	
43	856 m	852 m	862	13, Q; 17, ρ; 27 γ_1; 12 γ_2;	2
	848 m		842	ν_{43} at $\tau_2 = 30°$	
44	821w	828 w	844	100, ρ	2
45			844	100, ρ	1
46	820 m	818 m	815	30, ρ; 16, Q(C=O); 9, Q; 6, α	1
47	801 w	802 w	810	20, Q; 12, α; 25, ρ; 10 χ; 13,Q(C_{arom}-O)	1 1
48	755 s	750 s	740	42, ρ; 24, χ; 8, ρ(C_{arom}—O)	1
49	721 m		721	41, ρ; 28, χ; 16, ρ(C=O); 9, χ (CO)	1,2
50	708 s	710 vs.bd	708	80, ρ; 19, χ;	1
51	696 s	693 vs	703	56, ρ; 24, χ; 4, ρ(C_{arom}—O)	1,2
52	683 m	680 m	659	24, α; 14, ρ; 24, χ; 4, 10 γ_1	1,2
53	620 m	620 m	616	72, α; 21, β	1
54	618 sh		614	70, α; 22, β	2
55	575 m	575 m	558	46, α; 10, β; 13 γ_3	2
56	505 s	505 s	482	38, ρ; 34, χ; 7, β_3; 8, γ_2	1
57	452		461	28, χ; 11, ρ; 27, ρ(C_{arom}—O); 7, γ_1	2
58	448 sh		443	13, χ; 10, β_4; 13, γ_2	1,2
59	410 w		396	32, ρ; 68, χ	2
60			396	32, ρ; 68, χ	1
61	392		387	11, ρ; 25, χ, 25, β_4; 10, ρ(C=O)	1,2
	351		348	ν_{61} at $\tau_2 = 30°$	
62	310		290	42, γ_2; 16, β_4	1

Note. The symbols used for the notation of the vibrational coordinates of Ph^1 and Ph^2 are taken from Ref. 14.
The symbols used for the notation of the internal coordinates of EG are as follows: β_3 is $\angle C_{arom}C_{arom}O$; β_4 is $\angle C_{arom}C_{arom}C$; γ_1 is $\angle C_{arom}OC$; γ_2 is $\angle O{=}CO$; γ_3 is $\angle C_{arom}CO$.

mental data for benzaldehyde and acetophenone.[13b]

To sum up the results of the theoretical study of the conformations of the molecule, let us point out the following. First, the structure of PB predicted by the MM method fits the experimental data best. Second, the value of the barrier to internal rotation around the central C—O bond is about an order of magnitude greater than kT. This fact, as well as the difference in energy between the *cis*- and the *trans*-conformers, indicates that under normal conditions PB exists as the *trans*-conformer. The fairly low values of the barriers to rotation around τ_1 and τ_2 mean that the EG can be arranged in various directions around the benzene rings in accordance with the temperature and the aggregate state of the molecule. Note that the totally planar conformer and the structure with Ph^2 turned through 90° are defined in Ref. 5 as the most probably structures. This is in conflict with the experimental evidence as well as with the findings of the theoretical study of the molecule.

The investigation of the IR spectra of PB revealed that: 1) a great many more bands are observed in the spectrum of the crystal than in the spectra of the melt or of the solution; 2) the contours of the bands at 720, 1200, 1265, 1730 cm^{-1} and in the 1060 — 1080 cm^{-1} region are rather complex; 3) fast cooling causes some additional peaks to appear in the band at 1734 cm^{-1}. These peaks are missing from the spectra of the equilibrium crystal, but are present in the spectra of the solution and of the melt.

We connect these distinctions in the spectra with the possible realization of different values of τ_1 and τ_2 in the molecule. The dependence of the vibration frequencies on the rotation angle supports this view as follows. Calculations of the forms and frequencies of vibrations of the PB molecule showed that the vibrations of the two benzene rings hardly interact with each other (Table 2). Thus, most of the excess bands are due to the release of accidental degeneracy and to the presence of molecules with different structures in the elementary crystal cell.[6] The pairs of bands observed in the crystal spectrum are easy to assign to the individual vibrations of monosubstituted benzene rings[12,14]

According to our calculations the complex broad contours of some of the bands are due to the participation of polar oxygen bonds in the vibrations and may be caused by the superposition of several unresolved bands in the spectrum of the melt and several partially resolved bands in the spectrum of the crystal. The contribution of the C_{arom}—O coordinate to the vibrations at 800, 820, and 860 cm^{-1} is in line with other calculated data on the spectra of aromatic ethers.[15,16] Note that the band at 860 cm^{-1} is observed in the spectra of many low molecular weight aromatic esters and in the spectra of polyesters. The band is very sensitive to the structure and to phase changes, and has been assigned to EG vibrations (Table 2).

According to our calculations, the frequencies are hardly affected by changes in τ_1, but some of them are τ_2-sensitive (Table 3). The bands at 386 and 860 cm^{-1}, attributed to the vibrations of EG, shift the most (Table 3). In the experimental spectrum we observed frequencies with shifted values obtained by changing τ_2 from 67 to 30 ° (Tables 2, 3). This may be due to a situation in which two conformers with different τ_2 angles are fixed in the crystal.

Table 3. The dependence of the vibration frequencies on τ_2 angle

ν_m	90°	67°	30°	0°
ν_{20}	1326	1332	1340	1340
ν_{42}	919	915	909	908
ν_{43}	868	862	842	836
ν_{61}	411	387	348	325

The vibration at 915 cm^{-1} which depends slightly on the kinematics, is more responsive to changes in the value of $f_{(C_{arom}-O)/(C-H)}$. The splitting of the band in the crystal spectrum may be caused by the presence of two conformers with different values of $f_{(C_{arom}-O)/(C-H)}$ in the **F** matrix and, consequently, different frequency values, fixed in the crystal cell.

Let us consider the dependence of the of C=O stretching band at 1734 cm^{-1} on the temperature and the aggregate state. By the calculation, the mode is insensitive to changes in τ_1 and τ_2. The view seems to be justified since the vibration is highly characteristic. According to Mayants,[17] the degree of characterization is 97%. Hence, the changes in frequency of this vibration with changes in the angles depend only on the behavior of the F(C=O) force constant, which varies when the carboxyl group deviates from the plane of the phenyl ring due to changes in the electron density of the C=C bond. Using the following approximate scheme, let us try to estimate the magnitude of the F(C=O) change. Since the degree of π-conjugation is inversely related to cos τ_1, in the case of small angles, F(C=O) may be considered to be directly proportional to 1/cos τ_1. Then, with a 10° change in τ_1, F(C=O) ($18 \cdot 10^6$ cm^{-2}) changes only $0.27 \cdot 10^6$ cm^{-2} and ν(C=O) shifts by about 11 cm^{-1} because $\Delta\nu/\Delta F(C=O) = 41.6$ cm^{-1}. The order of magnitude of the shift correlates well with the experimental variations of ν(C=O).

According to experimental data,[18] the ν(C=O) value decreases as the degree of conjugation increases. Hence, the low frequency satellites in the spectra of the solution or the melt may be caused by the presence of the more planar configurations of the benzoate fragment of PB. Moreover, the ν(C=O) frequencies are known to be sensitive to the dielectric constant of the medium.[19] So the excess peaks on the contour of this band may result from intermolecular interactions. Thus, the splitting of the benzene bands and the appearance of conformation-sensitive bands on going to the crystal phase may be explained by the presence of PB molecules, arranged variously with respect to the axes of the crystal.

In conclusion, it should be noted that the PB spectra under conditions investigated are similar as a whole. The greater number of bands in the crystal spectrum as compared with the spectra of the melt and the solution is due to splitting of the bands and the realization of different angles of rotation of the phenyl rings. This suggests that the *cis*-form is lacking in the temperature interval covered. At 72 °C and when the energy difference between the conformers is 2.45 kcal/mol the content of the *cis*-form cannot exceed 3%, according to the Boltzmann factor. In the solution and in the melt the PB molecule has the extended *trans*-form close to that which it has in the crystal.

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