

VIBRATIONAL SPECTRA AND CONFORMATION OF MOLECULES OF DIPHENYL ETHER AND ITS DERIVATIVES AT LIQUID NITROGEN TEMPERATURE

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Differences between infrared spectra of crystalline samples of diphenyl ether and its derivatives measured at -180°C and the spectra of liquid samples measured at the laboratory temperature are explained by the hindrance of the internal rotation in molecules of the studied substances in the crystalline state at the low temperature.

Several years ago we published a paper on interpretation of the vibrational spectra of diphenyl ether and its 4-mono- and 4,4'-disubstituted derivatives¹ which was based on the concept of almost-free internal rotation in their molecules. We are attempting now to verify the validity of this concept by studying the infrared spectra of diphenyl ether and its derivatives at various temperatures and in various states of aggregation.

EXPERIMENTAL

Preparation and physical constants of diphenyl ether, its 4-fluoro, 4-chloro, 4-bromo, 4-iodo, 4,4'-dichloro, and 4-chloro-4'-bromo derivatives was described in the previous paper¹. The spectra of these compounds were obtained by means of the Perkin-Elmer 621 infrared spectrometer using a low-temperature cell with AgCl windows. Sample temperature was followed by means of a calibrated thermocouple down to -180°C . Infrared spectrum of diphenylether vapour was obtained in a heated cell with an optical pathlength of 10 cm and at a temperature about 100°C .

RESULTS AND DISCUSSION

The infrared spectra of liquid and gaseous diphenyl ether consist of a smaller number of rather broad bands and are mutually similar (Fig. 1 A, B). If we neglect the broadening of the gaseous sample bands due to the unresolved rotational structure of vibrational bands, the appearance of the spectra can be satisfactorily explained by a superposition of the spectra of all simultaneously populated conformations of the diphenyl ether molecule. However, the infrared spectrum substantially changes, if a crystalline sample of diphenyl ether (obtained by cooling the liquid sample in a low-temperature cell) is used in the measurements. The spectrum is characterized by

a large series of narrow bands which cannot be simply derived from the spectra of a liquid or a gaseous sample (Fig. 1C). Evidently, this is an intrinsic spectrum of a single conformation of the diphenyl ether molecule which represents complicated intramolecular interactions as well as crystal-field effects. The changes of the spectra are reversible, if the state and the temperature change. Analysis of a spectrum as complicated as the crystalline sample of diphenyl ether spectrum appears to be too complicated in view of the significance of information it offers. Therefore, we decided to confine ourselves to the interpretation of some parts of the spectrum only, and to a rather qualitative comparison of the spectra of samples in various states of aggregation. Table I summarizes an attempt to assign the bands over the region 1350 to 450 cm^{-1} of the spectrum of diphenyl ether in the gaseous, liquid, and crystalline state, respectively. The bands assigned in the spectra of the liquid sample¹ to the X-sensitive vibrations show a splitting resulting from the crystal-field effect; the bands of ring and adjacent hydrogen atoms vibrations split in a more complicated way. This is in agreement with the analysis of the liquid samples of diphenyl ether and its derivatives, where an accidental degeneration is expected for the other vibrations, but not for the X-sensitive ones. It is highly probable that the removal of an

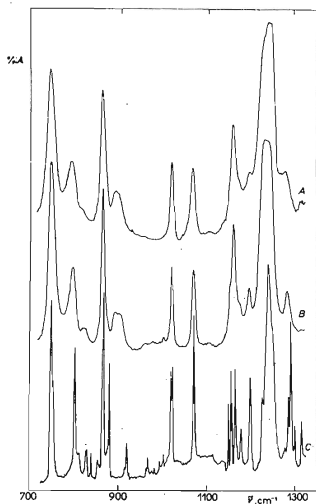


FIG. 1
Infrared Spectrum of Diphenyl Ether
A Gaseous at 100°C; B liquid at 40°C;
C crystalline at -180°C.

accidental degeneracy in the crystalline state hangs together with the existence of only one conformation of the diphenyl ether molecule (*e.g.*, of the Morino structure²) in which the two phenyl groups are non-equivalent (see discussion in ref.^{1,3}).

In the spectra of both the gaseous and liquid sample of diphenyl ether a broad and "fuzzy" band of the X-sensitive vibration e_1 at 1240 cm^{-1} dominates. Its parameters and "structure" make it possible to assume that thermally excited states of the bending vibration C—O—C from the far infrared region play a role. A similar situation was described in connection with an exceptional broadness and structure of the band of the antisymmetric stretching vibration Si—O—Si in hexamethyldisiloxane⁴. In the crystalline state these effects practically disappear.

A behaviour similar to that one of diphenyl ether exhibit its derivatives, too, and the same relations between liquid and crystalline samples were found in the spectra

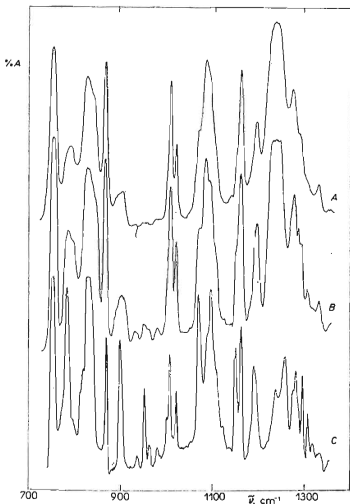


FIG. 2
Infrared Spectrum of 4-Chlorodiphenyl Ether

A Liquid at 40°C; B amorphous at -180°C; C crystalline at -180°C.

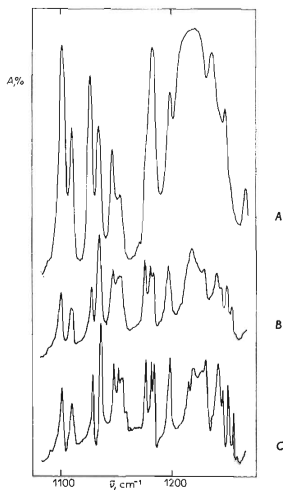


FIG. 3
Infrared Spectrum of 4-Iododiphenyl Ether

A Liquid at 50°C; B crystalline at 0°C; C crystalline at -180°C.

TABLE I

Wavenumbers $\nu(\text{cm}^{-1})$, Relative Intensities^a I , and Halfwidths $\Delta\nu_{1/2}(\text{cm}^{-1})$ of Bands from Infrared Spectra of Diphenyl Ether in Various States of Aggregation

Vibration assignment ^b	Vapour			Liquid			Crystal (-180°C)		
	ν	I^a	$\Delta\nu_{1/2}$	ν	I^a	$\Delta\nu_{1/2}$	ν	I^a	$\Delta\nu_{1/2}$
14, stretching CC	1 335	40	^c	1 334	27	14	1 335	18	8
	1 316	19	—	1 315	4	—	1 315	18	3
				1 303	—	—	1 300	14	3
3, δ CH bending	1 280	24	—	1 284	36	13	1 291	92	2
							1 286	20	<2 ^d
							1 278	—	—
e_1 , X-sensitive	1 243	710	27	1 238	688	23	1 250	—	—
							1 241	251	8
							1 227	10	—
e_2 , X-sensitive	1 198	8	—	1 198	32	7	1 200	47	5
							1 175	—	—
							1 178	14	4
9a, δ CH bending	1 162	140	13	1 163	171	9	1 165	49	2
							1 158	20	<2
							1 155	40	<2
9b, δ CH bending	1 106	—	—	1 108	4	12	1 150	29	<2
							1 070	100 ^e	12
							1 072	100 ^e	8
18b, δ CH bending	1 070	100 ^e	12	1 072	100 ^e	8	1 073	100 ^e	2
							1 022	108	8
							1 023	103	6
18a, δ CH bending	1 022	108	8	1 023	103	6	1 024	34	—
							1 020	32	—
							1 003	5	2
1 or 12, ring mode	1 005	—	—	1 003	7	3	997	—	—
							994	4	3
							982	—	—
5, γ CH bending	977	—	—	978	3	—	976	—	—
							967	5	2
							964	—	—
17a, γ CH bending	895	31	20	904	28	—	925	—	—
							920	12	3
							916	—	—
17b, γ CH bending	865	253	10	876	—	—	882	56	<2
							866	287	6
							867	139	<2
10a, γ CH bending	820	—	—	824	10	—	855	6	—
							840	10	<2
							831	6	—
d_1 , X-sensitive	794	64	20	797	79	12	828	5	—
							813	2	—
							803	67	4
d_2 , X-sensitive							754	13	—

TABLE I
(Continued)

Vibration assignment ^b	Vapour			Liquid			Crystal (-180°C)		
	ν	I^a	$\Delta\nu_{1/2}$	ν	I^a	$\Delta\nu_{1/2}$	ν	I^a	$\Delta\nu_{1/2}$
11, γ CH bending	747	320	15	747	420	12	749	108	3
							698	46	<2
							693	8	3
4, ring bending	690	316	13	690	439	9	688	121	3
				660	—	—	658	—	—
6b, ring bending	618	—	—	616	—	—	616	—	—
				603	—	—	603	4	3
c_1 , X-sensitive	565	—	—	563	—	—	563	9	3
b_1 , X-sensitive	490	45	—	497	60	—	498	59	3
16b, ring bending	477	30	—	476	52	—	476	21	5

^a Relative value of band extinction coefficient (with respect to the intensity of the band 18b); ^b numbering of vibrations and assignment, see ref.¹; ^c intensities and halfwidths for shoulders and strongly overlapping bands were not evaluated; ^d halfwidths of very narrow bands could not be reliably determined (Table listing as <2); ^e reference bands with extinction coefficient set to 100.

of all compounds studied by us. The 4-chloro derivative was used to appraise the significance of the state and temperature effects with respect to the conformation of molecules of the substances studied. This compound can be kept amorphous (the only one of the series) even at -180°C , if subjected to a rapid cooling. The spectrum of this sample is similar to that one of the liquid at 40°C , and differs markedly from the spectrum of the crystalline sample obtained in a slow cooling procedure (Fig. 2). It follows from this finding that the influence of the crystal field is primary; this can be confirmed with the 4-iodo derivative, too. This substance melts at 43°C , and thus spectra of its crystalline sample could be measured at two widely different temperatures, 0°C and -180°C . The spectra of both crystalline samples are to a large extent similar (the sample cooled to 0°C does not show such a good band resolution due to thermal effects) and differ from the spectrum of the melted sample at 50°C (Fig. 3).

The spectra of diphenyl ether and of its derivatives show that only for the crystalline samples measured at low temperatures it is meaningful to consider defined conformations. The behaviour of diphenyl ether in the gaseous and the liquid state can be better described by non-rigid models. These models also serve in interpreting NMR spectra^{5,6}, and in calculations of potential energy by means of quantum chemistry methods⁷.

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