[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS]

Absorption Spectra of Some Highly Substituted Diaryl Ethers

BY MURIEL DAHLGARD[1] AND RAY Q. BREWSTER

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The infrared and ultraviolet spectra of a large number of highly substituted derivatives of phenyl ether have been recorded. Large substituents at positions *ortho* to the ether oxygen atom greatly diminish significant absorption bands in both the infrared and ultraviolet regions. The latter are particularly indicative of hindrance to the molecule's assumption of a planar conformation.

Several groups of investigators[2,3] have studied the spectra of certain ethers in both the infrared and ultraviolet regions, but no extensive examination of the spectra of substituted diphenyl ethers has been reported in the literature. The present work was done in order to determine the variations in absorption spectra produced by the successive introduction of large substituents into various positions in the phenyl ether molecule. Of particular significance is a study of those derivatives of phenyl ether in which heavy atoms or groups of atoms replace the hydrogens at positions *ortho* to the oxygen linkage Such large substituents would be expected to interfere with rotation about the C–O–C bond and restrict coplanarity of the molecule with attendant steric inhibition of resonance between the aromatic nuclei and the unshared pairs of electrons on the oxygen atom. Burawoy and Chamberlain[3] were able to demonstrate the existence of this type of inhibition of resonance in substituted anisoles by the weakening of the absorption band at or near 270 mμ which is associated with the $-O-C_6H_5$ chromophore. The diminution of the intensity of this band in 2,4,6-trisubstituted anisoles is interpreted as evidence that the methyl group cannot easily come into the plane of the benzene ring. In the spectra of highly substituted diaryl ethers we find a direct continuation of this effect and, because of the presence of two aromatic nuclei in the ether molecule, a decided intensification of it. For example, in the ultraviolet spectrum of phenyl 2,4,6-trinitrophenyl ether (curve VII, Fig. 2) this band, associated with the quinonoid structure, is very weak and is lacking entirely in the spectrum of such ethers as 2,4,6-trinitrophenyl pentachlorophenyl ether (curve I, Fig. 2). Such observations suggest that the large substituents at positions *ortho* to the oxygen linkage may conceivably offer sufficient energy barriers to rotation that the isolation of optical antipodes may be possible; our attempt at the resolution of one highly substituted derivative of phenyl ether, however, was unsuccessful.[4]

Experimental

The aromatic ethers used in this work were prepared by the Ullmann reaction or by one of its well known modifications and require little comment. Highly substituted phenols, such as 2,4,6-trichlorophenol, do not react readily with *p*-nitrochlorobenzene in alkaline medium and with a copper catalyst, but aromatic ethers of this type may be obtained easily if the *p*-nitrochlorobenzene is replaced by *p*-nitrofluorobenzene or by 2,4-dinitrochlorobenzene. The picryl ethers were made by boiling a solution of picryl chloride, the phenolic compound and sodium ethoxide in absolute ethanol for about one hour. The melting points and analytical data for ethers not listed in the literature are shown in Table I.

The infrared spectra were taken with a Perkin–Elmer model 21 recording spectrophotometer. All solutions, unless otherwise indicated in the footnotes of the table, were 0.2 molar in carbon disulfide. The cell used had a thickness of 0.05 mm. In determining the molar absorptivities a reference line, corresponding to 100% transmittance, was drawn along the top of the chart and values of the molar absorbency index (ε) were then calculated from this line using the equation

$$\log I/I_0 = -\epsilon c d$$

where I is the intensity of the transmitted light, I_0 that of the incident light, c is the concentration in moles/liter and d is the path length in centimeters.

For the ultraviolet spectra a Beckman model DK recording spectrophotometer was employed using matched silica cuvettes of 1 cm. thickness. The concentration of solute in the 95% ethanol varied somewhat, as shown in Table I, because of limitations of solubility of some of the more highly substituted ethers.

Discussion

Infrared Spectra.—Significant portions of the infrared spectra of a few selected aromatic ethers are shown in Fig. 1. In this region the C–O–C asymmetrical stretching band at 1240 cm.$^{-1}$ is very prominent. Those ethers which contain a nitro substituent have a strong band, attributed to the symmetrical stretching of the nitrogen–oxygen bonds, at or near 1345 cm.$^{-1}$. Examination of these curves and of the data presented in Table II reveals these several generalizations: 1. A substituent at a position *ortho* to the ether oxygen atom weakens the ether absorption band (1240) and splits it into two closely adjacent bands. This formation of doublets, analogous to those observed in derivatives of anisole, suggests *cis* and *trans* conformations of the molecule. 2. A *p*-substituent has little influence upon the position or intensity of the ether band (1240). 3. An *o*-nitro group produces about the same shift in the position of the ether band as does an *o*-chlorine atom. The symmetrical stretching vibration of an *o*-nitro group (1345 cm.$^{-1}$) is much less intense than is that of its *p*-isomer because of the interference of the neighboring aromatic nucleus.[5] 4. All nitrated ethers

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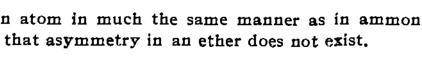
[1] The work reported in this paper is taken from the thesis submitted by Miss Dahlgard as part of the requirements for the degree of Doctor of Philosophy at the University of Kansas. It was presented at the Meeting of the American Chemical Society in Miami, Fla., April, 1957.

[2] H. E. Ungnade, E. E. Pickett, L. Rubin and E. Youse, *J. Org. Chem.*, **16**, 1318 (1951).

[3] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952).

[4] It is entirely possible, of course, that inversion may occur at



the oxygen atom in much the same manner as in ammonia and the amines so that asymmetry in an ether does not exist.

[5] We find an analogous type of absorption in comparing the spectrum of *p*-nitrochlorobenzene with that of its *o*-isomer; *cf.* R. J. Francel, THIS JOURNAL, **74**, 1268 (1952).

TABLE I

ABSORPTION SPECTRA OF HIGHLY SUBSTITUTED PHENYL ETHERS

				Carbon, %		Hydrogen, %		Halogen, %		Infrared spectra				Ultraviolet spectra	
										Nitro band		Ether band			
No.	R Substd. phenyl	R' Substd. phenyl	M.p., °C., or B.p. (mm.)	Found	Calcd.	Found	Calcd.	Found	Calcd.	Wave no., cm.$^{-1}$	ϵ_{max}	λ_{max} cm.$^{-1}$	$\epsilon_{max} \times 10^{-1}$	λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$
1	None	None										1240	87	279, 272, 265[9a]	17, 19, 16
2	2-Chloro	None	43.5	70.5	70.4	4.42	4.40	17.25	17.35			1245, 1270	57, 25	282, 276, 269[9a]	8, 17, 16
3	4-Chloro	None	149–152 (8)	70.1	70.4	4.34	4.40	17.27	17.35			1240	96	289, 279, 272[9a]	8, 15, 14
4	2-Chloro	4-Chloro	170–174 (8)	60.5	60.3	3.36	3.35	29.5	29.7			1245, 1265	55, 24	286, 276[9a]	12, 17
5	4-Chloro	4-Chloro	30	60.7	60.3	3.36	3.35	29.55	29.7			1240	77	290, 280, 273[9a]	15, 18, 18
6	2-Chloro	2,4-Dichloro	180–185 (6)	52.4	52.7	2.58	2.56	38.9	39.1			1245, 1262	26, 45	292, 282, 274[9a]	10, 18, 17
7	4-Chloro	2,4-Dichloro	51	52.5	52.7	2.34	2.56	38.9	38.9			1240, 1260	37, 70	294, 287, 277[9a]	9, 17, 19
8	2,4-Dichloro	2,4-Dichloro	72	47.0	46.8	2.08	2.00	45.9	46.1			1245, 1262	14, 37	292, 284[9a]	17, 23
9	2,4,6-Trichloro	2,4-Dichloro	36	42.1	42.0	1.39	1.46	52.1	51.8			1265, 1282	48, 11	291, 282[9a]	18, 20
10	2-Bromo	None										1240, 1265	45, 23	277, 270[9a]	20, 18
11	4-Bromo	None										1250	68	279, 272[9a]	15, 15
12	4-Bromo	4-Bromo										1235	84	290, 280, 273[9a]	15, 13, 18
13	4-Bromo	2,4-Dibromo	205–207 (2)					58.8	59.0			1240, 1255	44, 41	286, 276[9a]	22, 22
14	2-Nitro	None								1350	32	1245, 1265	58, 24	315, 255[9b]	28, 62
15	4-Nitro	None								1342	75	1250	111	303[9b]	115
16	2-Nitro	2-Phenyl	229–30 (4)	74.6	74.2	4.32	4.47	4.77[b]	4.82[b]	1350	28	1242, 1258	37, 37	310[9b]	20
17	4-Nitro	2-Phenyl	90	74.2	74.2	4.26	4.47	4.75[b]	4.82[b]	1350	69	1245, 1255	65, 57	280[9b]	85
18	2-Nitro	2-Chloro								1350	25	1250, 1270	48, 35	307, 255[9b]	23, 45
19	2-Nitro	4-Chloro								1360	27	1250, 1270	54, 22	317[9b]	20
20	4-Nitro-2-chloro	None	206 (6)			5.69[b]	5.63[b]	14.35	14.33	1350	65	1255, 1270	27, 105	308[9b]	88
21	4-Nitro	4-Chloro								1350	84	1252	125	302, 222[9a]	155, 170
22	2-Nitro	2-Bromo								1350	29	1245, 1262	48, 37	310, 260[9b]	18, 40
23	2-Nitro	4-Bromo								1358	24	1250, 1270	48, 20	318[9b]	18
24	2-Nitro	2,4-Dichloro	58			5.02[b]	4.93[b]	25.2	25.0	1348	29	1240, 1258	24, 51	318[9b]	23
25	4-Nitro	2,4-Dichloro								1340	65	1240, 1257	36, 75	292[9b]	122
26	4-Nitro	2,6-Dichloro	124			4.97[b]	4.93[b]	25.3	25.0	1340	75	1250	92	288[9b]	23
27	4-Nitro	2,4,6-Trichloro	106			4.47[b]	4.41[b]	33.4	33.5	1345	72	1260	66	288[9c]	138
28	2-Chloro-4-nitro	2,4,6-Trichloro	105			4.02[b]	3.96[b]	40.2	40.2	1347	70	1265	64	283[9c]	111
29	2,4-Dinitro	None								1345[8]	60	1275	62	293[9b]	140
30	2,4-Dinitro	2,4-Dichloro								1350	57	1250, 1275	7, 57	284[9b]	118
31	2,4-Dinitro	2,6-Dichloro	135			8.50[b]	8.52[b]	21.6	21.6	1345	59	1258, 1270	25, 59		
32	2,4-Dinitro	2,4,6-Trichloro	130[a]			7.70[b]	7.67[b]	29.3	29.2	1347	52	1270	49	274[9c]	118
33	2,4-Dinitro	2,4-Dibromo-6-phenyl	148			5.67[b]	5.65[b]	32.4	32.6	1345[8]	56	1247, 1265	24, 42		
34	2,4,6-Trinitro	None	152	47.2	46.7	2.30	2.43	13.8[b]	14.0[b]	1345[8]	45	1270	14	330[9a]	38
35	2,4,6-Trinitro	4-Chloro	114			12.6[b]	12.38[b]	10.1	10.43	1345[8]	60	1265	15	330[9c]	30
36	2,4,6-Trinitro	2,4-Dichloro	104			11.5[b]	11.2[b]	18.7	19.0	1345[8]	78	1270, 1290	23, 15	330[9c]	20
37	2,4,6-Trinitro	2,4,6-Trichloro	148			10.30[b]	10.28[b]	26.1	26.3	1345[8]	75	1260, 1285	15, 21	No band	
38	2,4,6-Trinitro	Pentachloro	195			8.80[b]	8.94[b]	37.2	37.9	1340, 1390[8]	56, 45	1240, 1280	12, 9	No band	

[a] Melting points of 122° and 136° for the compound are on record. [b] Nitrogen, %.

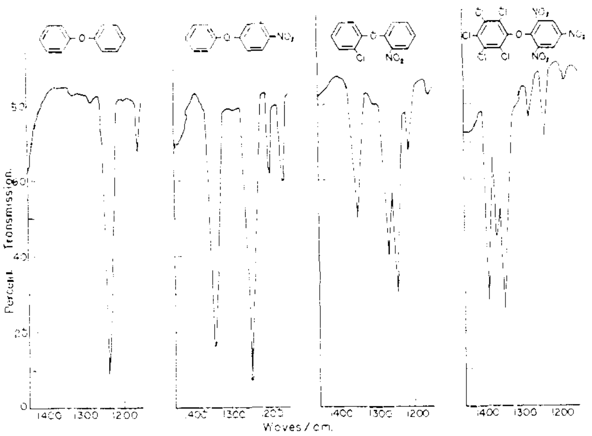


Fig. 1.—Portions of the infrared spectra of a few aromatic ethers showing the C–O–C stretching band of the ether group at 1240 waves cm.$^{-1}$ and that of the nitro group at 1345 waves cm.$^{-1}$. The solutions were 0.2 molar in carbon disulfide. The cell thickness was 0.05 mm.

included in this study have a broad fairly uniform band of absorption covering the range 1450 to 1580 cm.$^{-1}$ in which the asymmetric stretching band of the nitro group (catalogued at about 1520 cm.$^{-1}$) cannot be clearly detected. 5. In highly substituted ethers, such as the picryl ether of 2,4,6-trichlorophenol or of pentachlorophenol, the intensity of the ether band is much diminished.

Data pertaining to a number of highly substituted diphenyl ethers are given in Table I.[7–10]

Ultraviolet Spectra.—A few typical ultraviolet spectra of selected diaryl ethers are reproduced in Fig. 2; data for the spectra of these ethers as well as others are presented in Table I. Reference to Fig. 2 reveals that phenyl ether (curve VI) has strong absorption resulting in three peaks near 275 mμ (K band) associated with electronic contributions from the quinonoid structure. In 4-nitrophenyl phenyl ether (curve VIII) the strong absorption in this region (max. 303 mμ) may be an intensification of this band, though we regard it more likely that the strong absorption at 303 mμ represents a shift of the 220 mμ band of the parent phenyl ether according to the principles discussed by Doub and Vandenbelt.[6] In 4-nitrophenyl 2,4,6-trichlorophenyl ether (curve V) the band is still present but reduced in intensity presumably because the chlorine atoms *ortho* to the ether oxygen present a certain amount of hindrance to the coplanarity of the molecule required for resonance. Introduction of additional nitro groups into the molecule at positions *ortho* to the ether oxygen results in further inhibition of resonance with the consequence that the K band near 300 mμ, associated with the conjugation of the unshared electrons of the ether oxygen atom with the aromatic nuclei, is still further reduced in intensity. The picryl ether of *o*-cresol, for example, has been observed by other investigators[11] to show little absorption in this region, an observation well confirmed by the experiments here presented. In such compounds as the picryl ether of 2,4,6-trichlorophenol or that of pentachlorophenol (curves II and I, respectively) the absorption bands near 300 mμ are not detectable, indicating the high degree of resistance to coplanarity of the molecule offered by the large substituting groups. The data in Table I reveal the varying degrees of hindrance to coplanarity found in the other ethers studied.

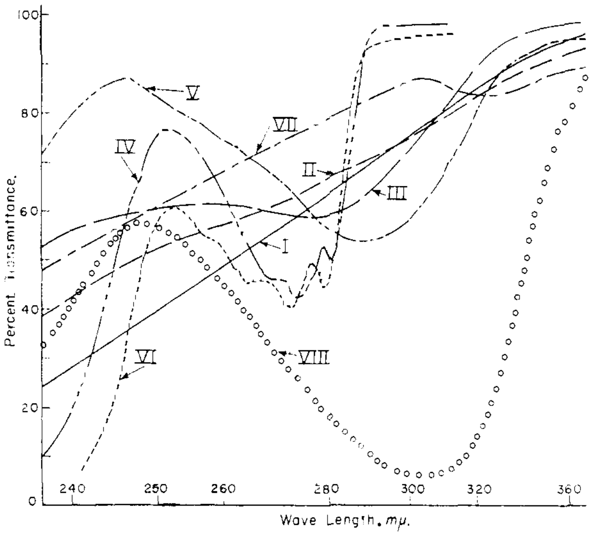


Fig. 2.—Ultraviolet spectra of some aromatic ethers: I, 2,4,6-trinitrophenyl pentachlorophenyl ether; II, 2,4,6-trinitrophenyl 2,4,6-trichlorophenyl ether; III, 2,4-dinitrophenyl 2,4,6-trichlorophenyl ether; IV, bis-2-chlorophenyl ether; V, 4-nitrophenyl 2,4,6-trichlorophenyl ether; VI, phenyl ether; VII, 2,4,6-trinitrophenyl phenyl ether; VIII, 4-nitrophenyl phenyl ether.

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[6] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

[7] Melting points and analytical data for compounds previously reported in the literature are omitted.

[8] Because of limited solubility in carbon disulfide, the concentration of the solution was 0.02 mole/liter. A cell of 0.5 mm. thickness was employed.

[9] The superscripts a, b, and c represent respectively concentrations of 2×10^{-4}, 1×10^{-4}, and 2×10^{-5} moles/liter in 95% ethanol. In all instances, cuvettes of 1 cm. thickness were used.

[10] For compounds that gave two or more peaks of maximum absorption the λ_{max} and ϵ_{max} values are reported in their respective orders. In compound no. 1, for example, the band at 1245 cm.$^{-1}$ has a ϵ_{max} value of 57×10^{-1} and that at 1270, an ϵ_{max} value of 25×10^{-1}.

[11] A. Cerniani, R. Rasserini and G. Richi, *Bull. Sci. fac. chim. ind. Bologna*, **12**, 7 (1954).