[Contribution from the Departments of Chemistry and Agricultural Chemistry, University of Missouri, and the Chemistry Department of New Mexico Highlands University]

ABSORPTION SPECTRA OF THE METHOXY (AND HYDROXY) PHENOXYBENZOIC ACIDS

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Ultraviolet absorption spectra have been determined for the 19 methoxy (and the corresponding hydroxy) phenoxybenzoic acids (1). For an evaluation of the data, absorption curves have also been prepared for the simple phenoxy-, methoxy-, and hydroxy-benzoic acids.[1]

It was ascertained some time ago that the light absorption of phenol and diphenyl ether is concentration dependent (2). Further work has now established that this may be true for anisole[2] but not for benzoic acid [*cf.* Braude (3)]. It is not surprising that similar deviations occur with hydroxy and methoxy acids. In the present investigation an effort has been made to determine all spectra in similar concentrations in order to minimize such deviations.

Methoxy and hydroxydiphenyl ethers possess nearly identical absorption spectra. Compared with diphenyl ether (2) these compounds show C-effects essentially undisturbed by steric effects, and loss in fine structure (Table I, Fig. 1). The red shifts due to the hydroxyl or methoxyl increase in the order $o < m < p$. The carboxylic acids of diphenyl ether (the phenoxybenzoic acids) present an entirely different picture. The introduction of the carboxyl group causes a large C-effect in the *o*- and *m*- position (Fig. 2). In the *para* acid only a single band of high intensity is observed. This is due to the large displacement of the short-wave benzenoid band and resultant superposition of the two bands. The maxima in these compounds are completely devoid of fine structure and the spectra are similar to those of the three methoxybenzoic acids (Table II, Fig. 3). The observed results do not entirely agree with the generalizations described in an abstract of a paper by Moser (4).[2a]

Methoxy (and hydroxy) phenoxybenzoic acids with the same structure would be expected to give similar curves barring a difference in the distribution of the electrons such as that produced by chelation. Such a relationship holds remarkably well for the 15 acids which do not have the two groups in adjacent positions (Table III).[3]

In the four *o*-hydroxy acids, hydrogen bonds occur between hydroxyl and carboxyl groups, which are absent in the corresponding methoxy acids. The *o*-quinoid resonance forms contribute significantly to the electronic structures

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[1] The ultraviolet absorption spectra were determined with a Model DU Beckman Spectrophotometer in 1-cm. silica cells.

[2] Anisole shows 3 maxima in ethanol at 220, 271, and 278 mμ (log ε 3.86; 3.24, and 3.20) and two minima at 238 and 275 mμ (log ε 1.80–1.84 and 3.11) in concentrations of 0.00004–0.0029 moles per liter (absorption spectra by John Mundzak, NMHU).

[2a] Note added in proof: They do agree, however, with conclusions reached in his recent paper, *J. Chem. Soc.*, 804 (1951).

[3] Small deviations in the extinction values of the maxima are due to concentration effects. These are particularly noticeable in the short wave region.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF HYDROXY AND METHOXYDIPHENYL ETHERS

SUBSTITUENT	MG./25 ML.[a]	λmax_1	LOG ε	λmin_1	LOG ε	λmax_2[b]	LOG ε	λmin_2	LOG ε	λmax_2	LOG ε
None	0.155	225	4.01	252	3.00	272	3.31	276	3.20	278	3.26
2-OH	.533	—	—	249	3.00	270	3.62	274	3.56	276	3.58
2-OCH_3	1.15	—	—	252	3.02	270	3.56	275	3.50	278	3.53
3-OH	0.219	—	—	253	3.10	273	3.50	276	3.48	280	3.48
3-OCH_3[c]	.38	—	—	253	3.01	273	3.49	276	3.47	278	3.48
4-OH	.58	230	4.10	259	3.27	281	3.48	286	3.46	288[e]	3.45
4-OCH_3[d]	.114	230	4.12	259	3.21	280	3.43	286	3.40	288[e]	3.40

[a] Solvent: cyclohexane containing 10% dioxane. [b] A submaximum occurs in diphenyl ether at 265 mμ (log ε 3.24) and in the 4-substituted compounds at 272 mμ (log ε 3.50 and 3.43). It is absent in the 2-hydroxy and 3-methoxy compounds and appears as a shoulder at 265 mμ in the remaining substances. [c] Absorption spectrum by John Mundzak, New Mexico Highlands University. [d] Absorption spectrum by Edward Kline, New Mexico Highlands University. [e] Shoulder.

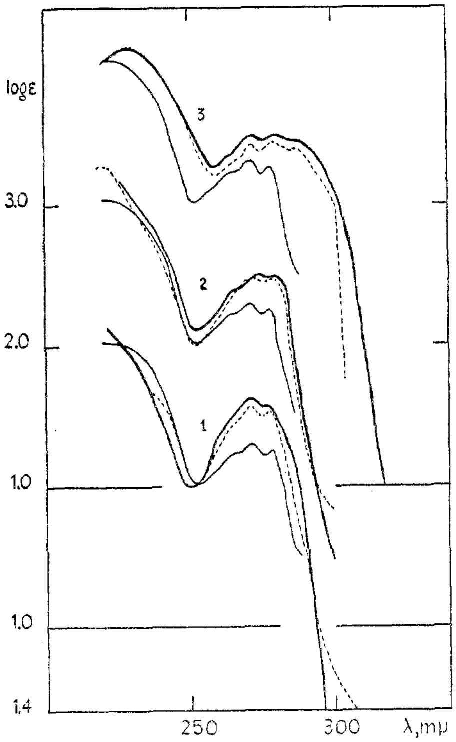


FIG. 1

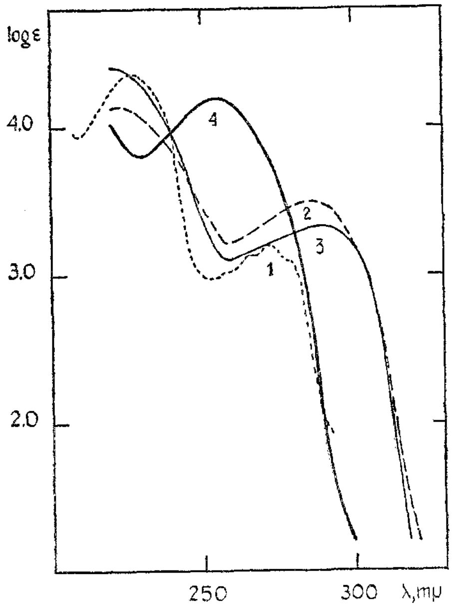


FIG. 2

FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA: ——— hydroxydiphenyl ether, --------- methoxydiphenyl ether, ——— diphenyl ether; 1, *ortho*; 2, *meta*; 3, *para*.

FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA: 1, benzoic acid; 2, *o*-phenoxybenzoic acid, 3, *m*-phenoxybenzoic acid; 4, *p*-phenoxybenzoic acid.

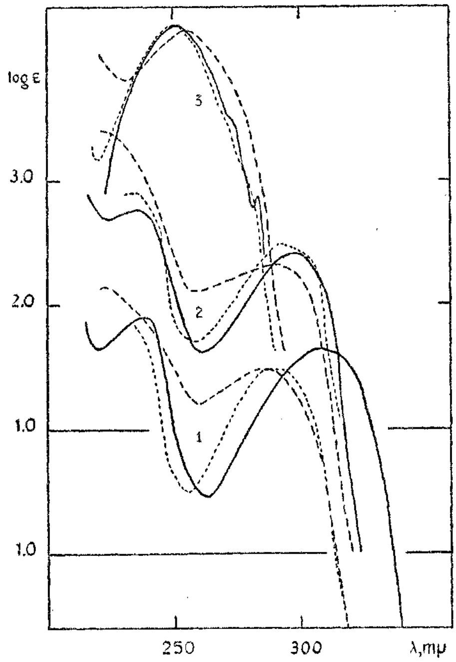


FIG. 3. ULTRAVIOLET ABSORPTION SPECTRA: ——— hydroxybenzoic acid, ---------- methoxybenzoic acid, — — — phenoxybenzoic acid; 1, *ortho*; 2, *meta*; 3, *para*.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF BENZOIC ACIDS

SUBSTITUENT	MG./25 ML.	λ_{max_1}	LOG ε	λ_{min}	LOG ε	λ_{max_2}	LOG ε
None[a]	—	228	—	255	—	273	—
2-OH[b]	0.25	237	3.90	264	2.48	308	3.64
2-OCH_3	.280[c]	—[e]	—[e]	256	2.50	291	3.49[d]
2-OØ	.632[c]	222	4.14	258	3.20	285	3.49
3-OH[b]	.25	235	3.76	261	2.62	298	3.40
3-OCH_3	.26[c]	234	3.89	258	2.70	292	3.49[d]
3-OØ	.627[c]	220	4.40	258	3.10	290	3.33
4-OH[b, f]	.0278	252	4.23	281	2.78	283	2.88
4-OCH_3[b]	.290	250	4.24[d]				
4-OØ	.505[c]	255	4.20				
2,3-di-OCH_3[b]	.241	—	—	262	2.85	294	3.42[e]

[a] Benzoic acid shows a short wave band in alcohol at 228 mμ (log ε 4.02). Its main band has a sharp maximum (273 mμ, log ε 2.94) and two pronounced shoulders (λ_{sh_1} 266, log ε 2.86 and λ_{sh_2} 280, log ε 2.86), concentration: 1.53×10^{-3}–2.65×10^{-5} moles/liter. In other solvents the shoulders resolve into bands (absorption spectra by Robert Lamb, NMHU). [b] Solvent: cyclohexane containing 10% ether. [c] Solvent: cyclohexane containing 10% dioxan. [d] Absorption spectra by Edward Kline, NMHU. [e] No maximum above 230 mμ. [f] *p*-Hydroxybenzoic acid has a minimum at 222 mμ (log ε 2.30). At 4.6×10^{-3} moles per liter the main band has two shoulders at 274 mμ and 284 mμ. The last one of these resolves into a distinct band at 2.0×10^{-5} moles per liter. (Absorption spectra by Robert Lamb, NMHU.)

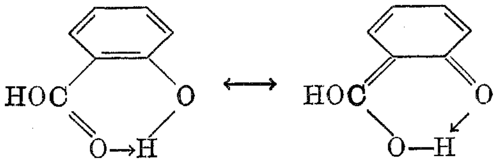
TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF HYDROXY (AND METHOXY) PHENOXYBENZOIC ACIDS

COOH	OH	OCH_3	CONC.[a] MG./25 ML.	λ_{max_1}[b]	LOG ε	λ_{max_2}	LOG ε	λ_{max_2}	LOG ε	λ_{max_2}	LOG ε
3	2		0.485	235	4.01	270	3.35	277	3.34	**316**[c]	3.70
3		2	1.34	235	3.86	270	3.39	277	3.38	**290**	3.35
4	2		0.548	251	4.07					**295**	3.72
4		2	1.14	260	3.99					**295**	3.73
5	2		0.527	**254**	4.18					285	3.44
5		2	0.203	**254**	4.00			278	3.58	285	3.45
6	2		0.515			269[d]	3.31	277	3.40	**297**	3.52
6		2	0.992			270	3.41	278	3.45	**295**	3.49
2′	2		0.646							**280**	3.68
2′		2	1.01							**280**	3.65
3′	2		0.481					**277**	3.62	300[d]	3.21
3′		2	0.91					**277**	3.59	300[d]	3.33
4′	2		0.702	**253**	4.30	270	3.98				
4′		2	1.00	**253**	4.15	270[d]	3.92				
2	3		0.636							**316**	3.76
2		3	1.06							**279**	3.54
4	3		0.461	**260**	4.20					**300**	3.82
4		3	0.61	**252**	4.08					**291**	3.69
5	3		0.572			270[d]	3.25	276[d]	3.20	**303**	3.55
5		3	1.04			271	3.31	278[d]	3.30	**301**	3.40
6	3		0.579	**252**	4.25			280[d]	3.46		
6		3	1.01	**249**	4.11			280[d]	3.38		
2′	3		0.561					**280**	3.60		
2′		3	0.980					**280**	3.62		
3′	3		0.412					**277**	3.56	300[d]	3.28
3′		3	[e]					—	—	—	—
4′	3		0.576	**255**	4.12					285[d]	3.60
4′		3	0.95	**255**	4.16					285[d]	3.53
3	4		0.582			272	3.26	278	3.24	**327**	3.58
3		4	0.940			272	3.29	277	3.28	**308**	3.53
2	4		0.572			272	3.22	277	3.22	**309**	3.50
2		4	1.00	238	3.91	272	3.24	277	3.24	**308**	3.51
2′	4		0.573							**290**	3.48
2′		4	1.09							**290**	3.65
3′	4		0.527					**285**	3.56	305[d]	3.38
3′		4	1.13					**285**	3.54	305[d]	3.35
4′	4		0.506	**256**	4.13					290[d]	3.51
4′		4	1.35	**258**	4.10					290[d]	3.50

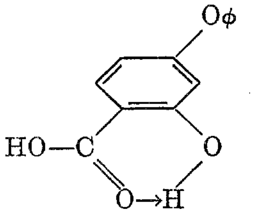
[a] Solvent: cyclohexane containing 10% dioxane. [b] The maxima are designated as λ_{max_1} and λ_{max_2} to indicate their probable assignment to the two fundamental bands in these compounds. Some uncertainty is involved in this assignment but the labelling is retained to facilitate comparisons. [c] Main absorption band in heavy print. [d] Shoulder. [e] Not determined.

and the spectra of the hydroxy acids are shifted to the red [on comparison with the main band of the corresponding methoxy acids (Fig. 4)]. The magnitude of the shift varies from 7.5 to 36 mμ. It is the strongest when the phenoxy group is adjacent to the chelate ring.

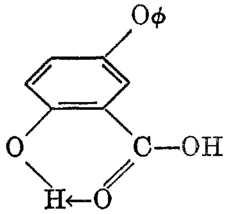


The spectral implication of an increased stability of the chelate ring is borne out also by the ionization constants of the acids which are in the order VIII > I > XVI > IX (5).

The presence of hydrogen bonds in the *o*-hydroxy acids is further indicated by the infrared absorption spectra of the compounds (Tables IV and V) which

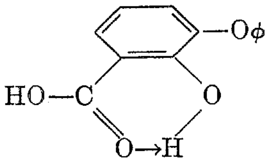


IX

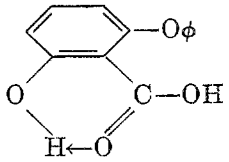


XVI

$\Delta\lambda_{\max}$ 7.5 19 mμ



I



VIII

$\Delta\lambda_{\max}$ 26 36 mμ

lack the absorption band at 3.0 μ and by the greatly increased K_a values of these acids, which are the strongest in this series (5).

While *o*-(*o*-hydroxyphenoxy)benzoic acid lactonizes easily (1), it does not have a hydrogen bond between hydroxyl and carboxyl groups. The ultraviolet absorption spectra of the acid and its methyl ether virtually coincide. The absence of a nine-membered chelate structure is also confirmed by the infrared data [Table V, compound (V)].

Ten of the acids under investigation may be regarded as phenoxy-substituted hydroxybenzoic acids (or methoxybenzoic acids). The introduction of the phenoxyl group into these acids should cause a bathochromic effect similar to methoxyl (but smaller), such as has been observed in a number of cases (6). Actually the electronic effects are more complex than in methoxyl, as is apparent from the study of the acidities in phenoxybenzoic acids by Dippy (7). The expected bathochromic shift of the main maximum (1–26 mμ) due to the phenoxyl group is observed in *o*- and *m*-hydroxy (and methoxy) benzoic acids when the phenoxy group is *ortho* or *meta* to the carboxyl group and when steric effects, discussed below, are absent. In the *para* position the phenoxy group causes a large bathochromic shift of the short wave maximum which then may or may not be superimposed on the main maximum. The latter is but slightly affected. The two phenoxy acids derived from *p*-hydroxy or methoxybenzoic acid show the same single maximum of the parent hydroxy acid. The effect of the phenoxy group is observed in a shoulder at about 290 mμ.

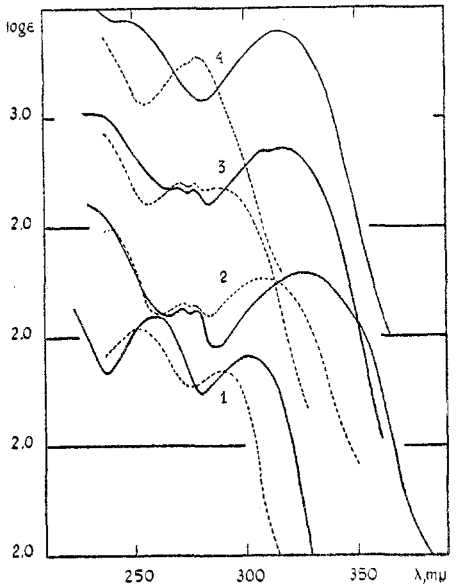


FIG. 4. ULTRAVIOLET ABSORPTION SPECTRA: ——— *o*-hydroxy acid, ---------- corresponding *o*-methoxy acid; 1, acid IX; 2, acid XVI; 3, acid I; 4, acid VIII.

TABLE IV

INFRARED ABSORPTION SPECTRA[a]

HYDROXYBENZOIC ACID	1ST BAND, μ	T, %	2ND BAND, μ	T, %
ortho	2.80	23.0	—	—
meta	2.82	18.0	3.03	9.0
para	2.80	5.5	3.05	5.5
DIPHENYL ETHER				
2-OH	2.80	6.5	2.97	4.0
3-OH	2.80	3.5	2.98	2.5
4-OH	2.80[b]	5.5	2.95	1.5
2-COOH	2.79	6.0	—	—
3-COOH	2.79	6.0	—	—
4-COOH	2.79	6.0	—	—

[a] In the range of 2.6–3.2 μ. [b] Shoulder.

Steric effects do not become noticeable in the long wave band of these acids as long as just one substituent group is adjacent to the carboxyl group [*cf* Ross (8)]. An exception is 3-phenoxy-2-methoxybenzoic acid. In this case the bathochromic effect due to the phenoxyl is absent and the extinction is slightly lower than in *o*-methoxybenzoic acid. Compared with *m*-phenoxybenzoic acid the maximum is actually at a lower wavelength ($\Delta\lambda_{\max}$ -20 mμ). There is no doubt therefore that the resonance of the carboxyl group with the ring is sterically hindered in this case. This is also true for 2-phenoxy-3-hydroxy and methoxybenzoic acid, but not for 3-phenoxy-2-hydroxybenzoic acid.[4]

TABLE V

INFRARED ABSORPTION SPECTRA OF THE HYDROXY PHENOXYBENZOIC ACIDS

	OH	COOH	1ST BAND, μ	T, %	2ND BAND, μ	T, %
I	2	3	2.79	8.5	—	—
II	2	4	2.80	5.5	3.05	1.0
III	2	5	2.81	4.5	3.05	1.0
IV	2	6	2.80	6.0	3.05	1.5
V	2	2′	2.80	4.0	3.05	2.0
VI	2	3′	2.80	4.0	3.05	2.0
VII	2	4′	2.81	5.0	3.05	2.0
VIII	3	2	2.80	8.0	—	—
IX	3	4	2.80	6.0	—	—
X	3	5	2.80	5.0	3.05	1.0
XI	3	6	2.79	7.5	—	—
XII	3	2′	2.80	6.6	—	—
XIII	3	3′	2.83	3.5	3.03	1.0
XIV	3	4′	2.80	5.5	3.04	1.0
XV	4	2	2.83[a]	5.5	3.03	1.0
XVI	4	3	2.80	7.0	—	—
XVII	4	2′	2.82	5.0	2.98	2.0
XVIII	4	3′	2.83[a]	6.0	3.00	1.5
XIX	4	4′	2.83	3.0	3.03	1.0

[a] Shoulder.

A pronounced steric effect is observed in 2-methoxy-6-phenoxybenzoic acid. Its main maximum is at a lower wavelength than that of either *o*-methoxy or *o*-phenoxybenzoic acid. The corresponding hydroxy acid does not appear to be hindered.[4]

The steric effectiveness of the groups is in the expected order OH $<$ OCH_3 $<$ OC_6H_5.

Inasmuch as the strongest absorption in the methoxy (and hydroxy) phenoxybenzoic acids is due to ArCOOH, the phenoxy acids with substituents in the phenoxyl group are best compared with the unsubstituted phenoxy acids. (Hydroxy and methoxy compounds of this type give virtually identical spectra.) Such a comparison shows that the introduction of a hydroxyl or methoxyl

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[4] Comparison is being made of one band, that which occurs closest to the visible region.

group into the phenoxy group causes either a bathochromic shift or the appearance of a broad band in the region of 265–290 mμ (where phenol or anisole absorb), or both (Fig. 5). In the *para* position, the oxygen causes a bathochromic shift of the main band. The effect is obscured in the *meta* phenoxy acid but is still recognizable in the curve (Fig. 5). The effects of *ortho* and *meta* hydroxy (or methoxy) substituents have proven to be very similar. The curves parallel those of the unsubstituted phenoxy acids in the region of the main maximum. A new absorption band appears at 270–280 mμ. This rather intense band determines the position of maximal absorption (λ_{max_2}) in the *o*- and *m*-phenoxy acids and appears as a shoulder in the *p*-phenoxy acid. It is concluded that the phenolic group may absorb independently except when the oxygen is in the *para* position. In this latter case, polarization effects are perhaps transmitted across the ether linkage (8).

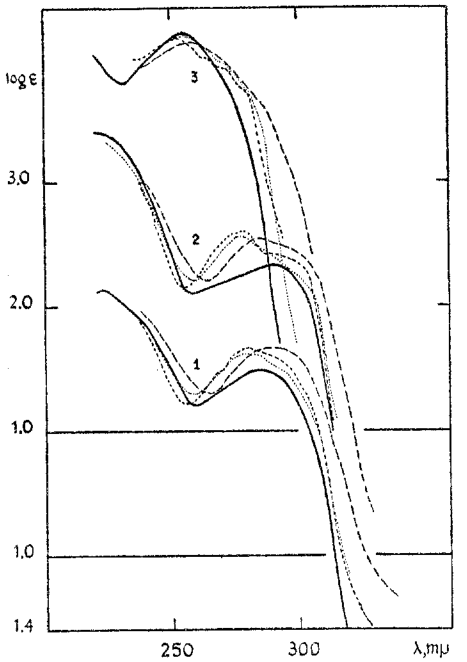

FIG. 5. ULTRAVIOLET ABSORPTION SPECTRA OF PHENOXY ACIDS: ——— phenoxybenzoic acid; ---------- *o*-methoxyphenoxy; .... *m*-methoxyphenoxy; — — — *p*-methoxyphenoxy; 1, *ortho*; 2, *meta*; 3, *para*.

In order to obtain evidence for hydrogen bonding in the compounds, infrared absorption spectra have been determined in dioxane in the range of 2.6–3.2 μ.[5] The three hydroxydiphenyl ethers show monomer hydroxyl bands at 2.8 μ and

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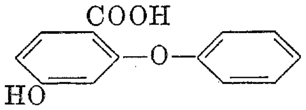
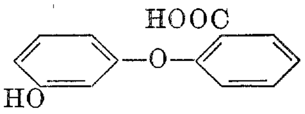
[5] Infrared absorption spectra were measured in 0.2 *M* dioxane solutions in 0.20-mm. cells against air in a Beckman IR-2 instrument. Unfavorable solubilities prevented determinations in other solvents.

polymer bands at 2.95–2.97 μ (10). The tendency for polymers appears greatest in the 4-isomer. The three carboxylic acids of diphenyl ether each show a single band of the same intensity at 2.79 μ. *m*- and *p*-Hydroxybenzoic acids each have the same monomer OH-bands at 2.80 and 2.82 μ and an intense polymer band at 3.04 and 3.03 μ, while salicylic acid possesses only a single band at 2.80 μ (Table IV).

In the hydroxy phenoxybenzoic acids (Table V), the 3.03-μ band is lacking in the established chelated acids (I, VIII, IX, XVI). It is, however, also absent in the acids XI and XII, both of which have the 3-hydroxyl group and the carboxyl group *ortho* to the ether linkage. Moreover, all six compounds, along with acids XIII and XIX, show very little absorption in the OH region in the crystalline state. The formation of polymers is evidently subject to other influences in addition to chelation and the absence of the 3.03-μ band cannot be regarded as critical evidence for chelation. The presence of this band, however, would make chelation rather unlikely.



XI



XII

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SUMMARY

Absorption spectra of 38 acids of diphenyl ether and related substances have been correlated with the structures of these compounds.

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