Semi-empirical Parameters in π-Electron Systems

VI. Heteroatomic Molecules Containing Ether-oxygen

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A modification of the Pariser-Parr-Pople method has been extended to mono- and disubstituted hydroxybenzenes, naphthols, cresols, furan, benzofuran, and mono- and disubstituted methylfurans. The method has been applied in calculations of bond lengths, ionization potentials, and electronic transitions.

1. INTRODUCTION

In a set of papers [1-5] it has been attempted to determine the semi-empirical parameters in the Pariser-Parr-Pople method in such a way that they can be used in arbitrary π-electron systems. Roos and Skancke determined the parameters for pure unsaturated hydrocarbons [1] and methylsubstituted ones,[2] Fischer-Hjalmars and Sundbom for nitrogen,[3] Grabe for chlorine,[4] and Jensen and Skancke for keto oxygen-containing molecules.[5] In this paper the method is extended to molecules containing ether-oxygen. The parameters have been determined through a least squares fit to the first ionization potential (IP) and the two lowest and three lowest of the four lowest singlet-singlet transitions of phenol and furan, respectively. The results have been tested on a set of molecules.

2. METHOD

The method has been described in the previous papers.[1-5] It is a SCF—MO—LCAO—CI method in the Pariser-Parr-Pople approximation. This means zero differential overlap (ZDO) and semi-empirical estimation of some integrals. It can be summarized as follows:

$$S_{\mu\nu} = \langle\mu|S|\nu\rangle = \delta_{\mu\nu} \tag{1}$$

$$\alpha_{\mu} = \langle\mu|H^{\text{core}}|\mu\rangle \neq 0 \tag{2}$$

$$\beta_{\mu\nu} = \langle\mu|H^{\text{core}}|\nu\rangle \begin{cases} \neq 0 \text{ when } \mu \text{ and } \nu \text{ are neighbours} \\ = 0 \text{ when } \mu \text{ and } \nu \text{ are not neighbours} \end{cases} \tag{3}$$

$$\langle \alpha\beta|r_{12}^{-1}|\mu\nu\rangle \;=\; \delta_{\alpha\mu} \; \delta_{\beta\nu} \; \gamma_{\mu\nu} \tag{4}$$

The core integral α_μ is calculated according to Goeppert-Mayer and Sklar [6]

$$\alpha_\mu \;=\; W_\mu - (n_\mu - 1)\gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_\nu \; \gamma_{\mu\nu} \tag{5}$$

where n_ν is the number of π-electrons on atom ν. Fischer-Hjalmars [7] has shown that the ZDO-approximation can be described as a second order theory in the overlap integral $S_{\mu\nu}$, between neighbours. The resonance integral $\beta_{\mu\nu}$ and the coulomb integral $\gamma_{\mu\nu}$ are local to the second order while W_μ is local only to the first order. To make the method consistent one should make W_μ dependent on the nearest neighbours to atom μ. This correction to W_μ as well as $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ between nearest neighbours depend on the bond length. Because of the small variation in length for the same type of bond in different molecules Roos and Skancke [1] assumed a linear dependence. The formulas are:

$$W_\mu \;=\; W_\mu{}^0 + \sum_\nu \Delta W_\mu(\nu) \tag{6}$$

$$\Delta W_\mu(\nu) \;=\; \Delta W_\mu{}^0(\nu) + \delta_{\mu\nu}{}^W (R_{\mu\nu} - R_{\mu\nu}{}^0) \tag{7}$$

$$\beta_{\mu\nu} \;=\; \beta_{\mu\nu}{}^0 + \delta_{\mu\nu}{}^\beta (R_{\mu\nu} - R_{\mu\nu}{}^0) \tag{8}$$

$$\gamma_{\mu\nu} \;=\; \gamma_{\mu\nu}{}^0 + \delta_{\mu\nu}{}^\gamma (R_{\mu\nu} - R_{\mu\nu}{}^0) \tag{9}$$

In these formulas atom ν is a nearest neighbour to atom μ and $R_{\mu\nu}{}^0$ is a chosen standard length for the bond $\mu\nu$.

The one-center integrals $\gamma_{\mu\mu}$[8] have been taken from spectral data, while the integrals $\gamma_{\mu\nu}$ between non-neighbours have been calculated with the ball approximation.[9]

The calculations have been done with a SCF—MO computer programme written by P. Eisenberger, T. Alm and B. Roos. It calculates the ground state with a single determinant and the energy levels of the excited states by mixing all singly excited states. The programme gives also the π-electron dipole moment.

3. CARBON PARAMETERS

The carbon parameters $W_C{}^0$, $\Delta W_C{}^0(C)$, $\delta_{CC}{}^W$, $\beta_{CC}{}^0$, $\delta_{CC}{}^\beta$, $\gamma_{CC}{}^0$, $\delta_{CC}{}^\gamma$ and γ_{CC} have been given in Refs. 1, 2. They are listed in Table 1. The standard carbon-carbon distance is the bond length 1.397 Å in benzene, $W_C{}^0$ is the IP for the π-orbital in the planar CH_3 radical. The expression $\Delta W_C{}^0(C) + \delta_{CC}{}^W(R_{CC} - R_{CC}{}^0)$ is the correction to $W_C{}^0$ when an sp^2 hybridized carbon atom has replaced a hydrogen atom. The diameter of the balls for carbon in the ball approximation is 1.47 Å.

4. METHYL PARAMETERS

Roos [2] determined the parameters W_{CH_3}, $\Delta W_C(CH_3)$, β_{C-CH_3}, γ_{C-CH_3}, and $\gamma_{CH_3CH_3}$ for the methyl group. The C—CH_3 bond length is assumed to be constant. The values are listed in Table 1. The methyl diameter in the ball approximation is 1.76 Å.

Table 1. Semi-empirical parameters for heteroatomic molecules containing ether-oxygen.

Carbon π-parameters [2]		Methyl parameters [2]		Present work:ether oxygen parameters	
R_{CC}^0	= 1.397 Å	$\gamma_{CH_3CH_3}$	= 10.01 eV	R_{CO}	= 1.35 Å
γ_{CC}	= 11.97 eV	γ_{C-CH_3}	= 5.70 eV	γ_{OO}	= 18.89 eV
γ_{CC}^0	= 6.91 eV	β_{C-CH_3}	= − 1.38 eV	γ_{CO}	= 6.20 eV
δ_{CC}^γ	= −3.99 eV/Å	W_{CH_3}	= −12.02 eV	β_{CO}	= − 1.80 eV
β_{CC}^0	= −2.42 eV	$\Delta W_C(CH_3)$ =	0.50 eV	W_O^0	= −11.18 eV
δ_{CC}^β	= 3.05 eV/Å			$\Delta W_O(C)$ =	1.51 eV
W_C^0	= −9.84 eV			$\Delta W_C(O)$ =	− 0.09 eV
$\Delta W_C^0(C)$ =	0.07 eV				
δ_{CC}^W	= 9.22 eV/Å				

5. OXYGEN PARAMETERS

To determine the oxygen parameters phenol and furan have been used as standard molecules. As the assumed carbon-oxygen distances in the two molecules differ only by 0.012 Å, no bond length dependence has been included. That left the following parameters: W_O^0, $\Delta W_O(C)$, $\Delta W_C(O)$, β_{CO}, γ_{CO} and γ_{OO}. The one-center integral γ_{OO} was determined from spectral data [8] in the same manner as γ_{CC}. The other parameters were determined through a least squares fit to the first IP and three of the four lowest singlet-singlet transitions of furan and the first IP and the two lowest singlet-singlet transitions of phenol. Preliminary calculations showed that the result was quite insensitive to changes in γ_{CO}, so this integral was given the reasonable value 6.2 eV in the beginning of the calculations and after that only the other four parameters were varied. The resulting parameter set is given in Table 1. The oxygen diameter in the ball approximation is 1.04 Å.

6. EXPERIMENTAL DATA FOR STANDARD AND TEST MOLECULES

Unfortunately the experimental data for the considered molecules are far from complete.

Geometry. Bak *et al.*[10] have determined the geometry of furan very accurately by microwave spectroscopy. This geometry has also been used on the methylsubstituted furans. The CH_3 group was placed on the bisector to the angle at the corresponding carbon atom and at the distance used in the paper by Roos.[2]

For phenol and the disubstituted benzenes a regular benzene ring[11] was assumed. The CH_3 group was treated in the same way as in the methylfurans. Bacon and Curry[12] give the carbon-oxygen distances in resorcinol as 1.34 Å and 1.36 Å in a neutron diffraction experiment. In this paper the mean distance $R_{CO} = 1.35$ Å and the angle $\angle CCO = 120°$ were taken for these molecules. Many workers have used $R_{CO} = 1.36$ Å, but as no distance dependence is included in $\Delta W_C(O)$, $\Delta W_O(C)$, β_{CO}, and γ_{CO}, a small variation in R_{CO} changes only the coulomb integrals calculated with the ball approximation very little and has little influence on the final results.

No data on the naphthols were found, so they were assumed to consist of two regular benzene rings and an OH group as in the phenol case. Almenningen et al.[13] have determined the naphthalene structure and their results have been included as a comparison.

Lastly, benzofuran was built by a benzene ring and a furan ring, in which the appropriate C—C bond was opened to 1.397 Å.

Ionization potentials. The calculated IP's correspond to vertical values. Most IP's found in the literature are adiabatic values, however, which are somewhat lower than the vertical ones. Turner [14] has published very accurate adiabatic IP's measured by photoelectron spectroscopy for phenol, furan, 2-methylfuran, and 2,3-dimethylfuran. Turner et al.[15] have also recently published the vertical IP of phenol. The carbon and methyl parameters have been determined by fitting to adiabatic values, so this has been done in this paper too.

Crable and Kearns [16] have measured the IP's of phenol and the cresols by mass-spectrometric methods. For the other molecules no experimental IP's seem to be available.

Electronic transitions. The calculated singlet-singlet transitions correspond to vertical transitions in the gas phase. Very few experimental papers give the absorption maxima in the gas phase.

The singlet-singlet transitions in furan were fitted to the vapour UV-spectrum by Pickett.[17,18] The peak around 52 230 cm^{-1} has been interpreted as a Rydberg transition,[27] so the four lowest $\pi—\pi^*$ transitions were taken at ~46 000, 48 900, 59 600 and 62 800 cm^{-1}. Price and Walsh [19] and Watanabe [20] have also published vapour phase spectra for furan. For the methylfurans no spectra were found.

The ^1L_b and ^1L_a transitions of phenol were fitted to the vapour phase spectrum by Kimura and Nagakura.[21] To compare the series phenol, the di-
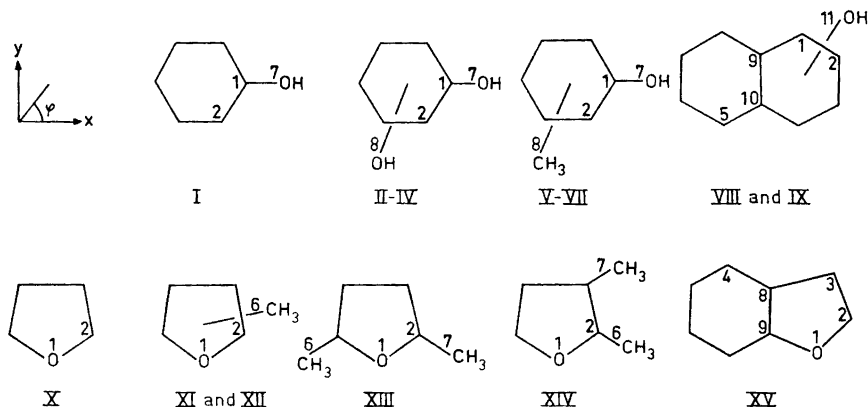

Fig. 1. Choice of coordinates and polarization angle φ, as well as numbering of the atoms in the molecules. I: Phenol; II: Hydroquinone; III: Resorcinol; IV: Pyrocatechol; V: p-Cresol; VI: m-Cresol; VII: o-Cresol; VIII: α-Naphthol; IX: β-Naphthol; X: Furan; XI: 2-Methylfuran; XII: 3-Methylfuran; XIII: 2,5-Dimethylfuran; XIV: 2,3-Dimethyl-furan; XV: Benzofuran.

hydroxybenzenes and the cresols, three other papers have been used. Kiss et al.[22] give the ^1L_b band for phenol, the dihydroxybenzenes, and the cresols in ethanol. Dearden and Forbes [23] give both the ^1L_b and the ^1L_a bands for the same molecules in cyclohexane. Klevens and Platt [24] give the ^1L_a, ^1L_b, and ^1B bands for phenol, the cresols and hydroquinone in heptane. In the same paper they have a graph of the benzofuran spectrum without interpretation. In this case the band maxima were estimated from the graph. Finally Baba and Suzuki [25] have published the spectra of the naphthols in isooctane.

7. RESULTS AND DISCUSSION

Bond orders and bond lengths. The bond orders are given in Tables 2—4.
The carbon-carbon distances (Tables 2—4) have been calculated by the relation [26]

$$R_{\mu\nu} = 1.517 - 0.18 \; p_{\mu\nu} \tag{10}$$

where $R_{\mu\nu}$ is the distance in Å between atoms μ and ν and $p_{\mu\nu}$ is the mobile bond order. To get a similar relation for R_{CO} is more difficult. Here the following formula [27] has been used

$$R_{CO} = 1.430 - 0.214 \; p_{CO} \tag{11}$$

For phenol, the dihydroxybenzenes, and the cresols there are some interesting points. The deviations from the assumed benzene geometry are less than 0.007 Å. The deviations occur in bonds where an OH group or a CH_3 group is attached to one or both carbon atoms in the bond. The deviation due to the OH group is around +0.004 Å and it is around +0.002 Å for the CH_3 group. Another interesting point is the carbon-oxygen distance in phenol. The calculated value 1.376 Å is larger than the assumed value 1.35 Å. But the calculated

Table 2. Calculated and observed bond distances in phenol and furan. Distances in Å. The numbering of the atoms is given in Fig. 1.

Molecule	Bond	Bond order	Bond length		
			Calc.	Obs.	
Phenol	2—1	0.645	1.401	1.395 [a 28]	1.395 [a 29]
	3—2	0.670	1.396	1.395	1.395
	4—3	0.665	1.397	1.395	1.395
	7—1	0.251	1.376	1.379	1.367—1.369
Furan	2—1	0.408	1.343	1.362 [10]	
	3—2	0.829	1.368	1.361	
	4—3	0.497	1.428	1.431	

[a] Regular hexagon assumed.

Table 3. Calculated bond distances. Distances in Å. The numbering of the atoms is given in Fig. 1.

Bond	Bond order	Calc. bond length	Bond	Bond order	Calc. bond length
Hydroquinone			**2-Methylfuran**		
2−1	0.645	1.401	2−1	0.412	1.342
3−2	0.671	1.396	3−2	0.823	1.369
7−1	0.244	1.378	4−3	0.492	1.430
			5−4	0.832	1.367
			5−1	0.390	1.347
Resorcinol			6−2	0.138	
2−1	0.648	1.400			
4−3	0.643	1.401			
5−4	0.668	1.397	**3-Methylfuran**		
7−1	0.252	1.376			
			2−1	0.385	1.348
			3−2	0.825	1.368
Pyrocatechol			4−3	0.491	1.429
			5−4	0.827	1.368
2−1	0.627	1.404	5−1	0.411	1.342
3−2	0.651	1.400	6−3	0.136	
4−3	0.666	1.397			
5−4	0.665	1.397			
7−1	0.239	1.379	**2,5-Dimethylfuran**		
			2−1	0.395	1.346
			3−2	0.829	1.368
p-Cresol			4−3	0.484	1.430
2−1	0.646	1.401	6−5	0.133	
3−2	0.669	1.397			
4−3	0.658	1.399			
7−1	0.244	1.378			
8−4	0.144		**2,3-Dimethylfuran**		
			2−1	0.392	1.346
			3−2	0.823	1.369
m-Cresol			4−3	0.491	1.429
2−1	0.647	1.401	5−4	0.828	1.368
3−2	0.661	1.398	5−1	0.394	1.346
4−3	0.656	1.399	6−2	0.127	
5−4	0.666	1.397	7−3	0.125	
6−5	0.669	1.397			
6−1	0.644	1.401			
7−1	0.253	1.376	**Benzofuran**		
8−3	0.148				
			2−1	0.373	1.350
			3−2	0.863	1.362
o-Cresol			5−4	0.708	1.389
			6−5	0.627	1.404
2−1	0.639	1.402	7−6	0.703	1.391
3−2	0.664	1.397	8−3	0.413	1.443
4−3	0.664	1.398	8−4	0.588	1.411
5−4	0.666	1.397	9−1	0.352	1.355
6−5	0.666	1.397	9−7	0.604	1.408
6−1	0.650	1.400	9−8	0.604	1.408
7−1	0.237	1.379			
8−2	0.141				

Table 4. Calculated distances in α-naphthol and β-naphthol compared to the observed structure of naphthalene. Distances in Å. The numbering of the atoms is given in Fig. 1.

Bond	Bond order		Calc. bond length		Obs. in naphthalene [13]
	α	β	α	β	
2−1	0.720	0.722	1.387	1.387	1.371
3−2	0.588	0.564	1.411	1.415	1.412
4−3	0.743	0.750	1.383	1.382	1.371
6−5	0.744	0.744	1.383	1.383	1.371
7−6	0.585	0.584	1.412	1.412	1.412
8−7	0.743	0.745	1.383	1.383	1.371
9−1	0.516	0.536	1.424	1.420	1.422
9−8	0.539	0.534	1.420	1.421	1.422
10−4	0.532	0.531	1.421	1.421	1.422
10−5	0.535	0.536	1.421	1.421	1.422
10−9	0.552	0.550	1.418	1.418	1.420
11−1,2	0.259	0.253	1.375	1.376	

phenol structure is supported by microwave determinations by Forest and Dailey [28] and Quade.[29] Forest and Dailey get $R_{CC} = 1.3954$ Å and $R_{CO} = 1.379$ Å as the most likely structure. Quade uses the ring structure by Forest and Dailey and gets two different phenol structures, in the first one $R_{CO} = 1.367$ Å and in the second one $R_{CO} = 1.369$ Å. This is in line with the calculated relative magnitudes of the bond orders for the CO bonds in phenol and furan. The bond orders clearly indicate that the bond in phenol is longer than that in furan, opposite to what was assumed. Unfortunately the author was not aware of these two papers before the calculations were already done.

Table 5. Calculated and observed π-electron densities of furan and benzofuran. The numbering of the atoms is given in Fig. 1.

Molecule	Atom	Calc. density	Obs. density [30]
Furan	1	1.741	1.933
	2	1.083	0.995
	3	1.046	1.038
Benzofuran	1	1.777	1.859
	2	1.072	1.001
	3	1.053	1.027
	4	0.990	0.985
	5	1.016	1.017
	6	0.998	1.008
	7	1.045	1.016
	8	1.035	1.043
	9	1.015	1.044

Table 6. Calculated π-electron densities. The numbering of the atoms is given in Fig. 1.

Molecule	Atom	π-Electron density	Molecule	Atom	π-Electron density
Phenol	1	0.989	α-Naphthol	1	0.989
	2	1.034		2	1.044
	3	0.995		3	0.994
	4	1.015		4	1.022
	7	1.937		5	1.001
				6	1.001
Hydroquinone	1	1.003		7	1.005
	2	1.028		8	1.009
	7	1.940		9	1.013
				10	0.990
Resorcinol	1	0.985		11	1.932
	2	1.069			
	4	1.049	β-Naphthol	1	1.045
	5	0.990		2	0.990
	7	1.937		3	1.027
				4	0.995
Pyrocatechol	1	1.020		5	1.002
	3	1.029		6	1.007
	4	1.010		7	1.002
	7	1.941		8	1.004
				9	0.989
p-Cresol	1	1.004		10	1.002
	2	1.030		11	1.936
	3	1.032			
	4	0.951	2-Methylfuran	1	1.753
	7	1.940		2	1.016
	8	1.980		3	1.100
				4	1.043
m-Cresol	1	0.987		5	1.108
	2	1.072		6	1.981
	3	0.932			
	4	1.052	3-Methylfuran	1	1.749
	5	0.992		2	1.138
	6	1.050		3	0.986
	7	1.936		4	1.065
	8	1.979		5	1.080
				6	1.982
o-Cresol	1	1.025			
	2	0.968	2,5-Dimethyl-	1	1.763
	3	1.033	furan	2	1.040
	4	1.012		3	1.097
	5	1.010		6	1.982
	6	1.030			
	7	1.942	2,3-Dimethyl-	1	1.759
	8	1.981	furan	2	1.069
				3	1.039
				4	1.061
				5	1.106
				6	1.983
				7	1.984

Table 7. Dipole moments. Calculated value of μ_π, in Debye. The angle φ is defined in Fig. 1.

Molecule	Calc. μ_π	φ
Phenol	0.74	0°
Hydroquinone	0.0	
Resorcinol	0.73	−60°
Pyrocatechol	1.21	−30°
p-Cresol	0.15	0°
m-Cresol	0.67	−46°
o-Cresol	1.08	−26°
α-Naphthol	0.80	+89°
β-Naphthol	0.85	+18°
Furan	1.58	−90°
2-Methylfuran	1.98	−74°
3-Methylfuran	1.07	−84°
2,5-Dimethylfuran	2.22	−90°
2,3-Dimethylfuran	1.53	−66°
Benzofuran	1.40	−59°

Table 8. Calculated and observed ionization potentials. Values given in eV.

Molecule	Calc.	Obs.	
		Turner [14]	Crable and Kearns [16]
Phenol	8.45	8.46 [a,b]	9.16
	9.14	9.34	
	10.75		
	12.55		
Hydroquinone	7.92		
Resorcinol	8.16		
Pyrocatechol	8.08		
p-Cresol	8.16		8.97
m-Cresol	8.32		8.98
o-Cresol	8.29		8.93
α-Naphthol	7.64		
β-Naphthol	7.78		
Furan	8.78	8.77 [a]	
	9.42	(10.21)	
	12.30	12.62	
2-Methylfuran	8.39	8.31	
3-Methylfuran	8.52		
2,5-Dimethylfuran	8.03		
2,3-Dimethylfuran	8.12	8.01	
Benzofuran	8.12		

[a] Data used for parameter determination.
[b] Vertical value 8.75 eV, Turner *et al.*[15]

For the naphthols it is seen that ring structures do not deviate much from the naphthalene structure. The previously mentioned elongation of the C—C bond due to the OH group is observed here too.

In furan the C—C bonds are very well reproduced in the calculations while the C—O bond is too short. Even though the formula (11) is uncertain the bond order is too large.

For the methylfurans and benzofuran only the assumed and the calculated values are given.

π-Electron densities. The densities are listed in the Tables 5 and 6. The only experimental values are those for furan and benzofuran by Black *et al.*[30] They have studied what corrections should be made to correlate proton chemical shifts to π-electron densities. Their value for oxygen in furan is surprisingly high compared to their values for other heteroatoms.

Dipole moments. The π-electron contributions to the dipole moments are given in Table 7.

Ionization potentials. The IP's are calculated with Koopmans' theorem, which means that they should be compared to the vertical IP's. However, the parameters were determined through fitting to adiabatic values. With this in mind it is interesting to compare experiment and calculation (Table 8). For both phenol and furan the lowest IP was reproduced almost exactly. It is reasonable to believe that the differences between adiabatic and vertical values in furan, 2-methylfuran, and 2,3-dimethylfuran are of the same magnitude. As Turner [14] has given accurate values for all three molecules it should be possible to see how well the parameter set reproduces the substituent effects. The differences between calculated and observed values are +0.01, +0.08 and +0.11 eV which is quite satisfactory.

For the cresols the calculated values should not be compared directly to those by Crable and Kearns.[16] Instead, the differences in the phenol and cresol series should be compared. The fit is fairly good, though the relative order is not reproduced exactly. The IP's of the other molecules seem to be in a reasonable range. The higher IP's are given only for furan and phenol, where there are experimental values for comparison. The second IP of furan is very uncertain and it is not possible to draw any conclusions about the higher IP's here.

Electronic transitions. The calculated and observed transitions have been collected in Tables 9—12.

The spectra of the standard molecules are well reproduced. This is very satisfactory, since the interpretation of the furan spectrum is a difficult question. With the parameter set adopted in this paper it has been possible both to reproduce the assumed furan spectrum and to predict many other properties in several different molecules.

For the series phenol, dihydroxybenzenes, and cresols both calculation and experiment show two things. Firstly, phenol has the highest frequency in all bands. Secondly, in the ^1L_b band substitution in the *para* position gives more red-shift than in the *ortho* and *meta* positions.

There is also good agreement between calculation and experiment for the relative order of the first two transitions in the naphthols. The first transition has higher frequency and the second one lower frequency in α-naphthol than

Calculation			Kimura and Nagakura[21] vapour			Observations						
						Dearden[23] cyclohexane		Kiss et al.[22] ethanol		Klevens and Platt[24] heptane		
ν	f	pol	ν_{max}	range	f	ν_{max}	log ε	ν_{max}	log ε	ν_{max}	range	log ε
Phenol												
37.90	0.013	y	37.0[a]		0.020	37.2	3.34	36.4	3.32	36.7	35—42	3.18
47.06	0.158	x	46.9[a]	44—51	0.132	47.6	3.78			47.0	42—49	3.78
53.69	0.830	y	54.0	51—57	0.636					52.7	49—57→	4.70
54.72	1.036	x	55.9	53—60	0.467							
Hydroquinone												
36.54	0.041	y				34.2	3.46	33.4	3.35	43.7	42—46	3.74
44.97	0.275	x				44.8	3.64			52.6	48—55→	4.45
53.35	0.828	y										
54.66	1.064	x										
Resorcinol												
37.08	0.011	+30°				36.5	3.33	36.1	3.34			
45.59	0.067	−60°				46.1	3.83					
51.53	1.088	+30°										
51.95	0.736	−60°										
Pyrocatechol												
36.93	0.017	−30°				36.5	3.40	36.0	3.42			
44.79	0.105	+60°				46.7	3.83					
52.00	1.061	−30°										
52.36	0.753	+60°										
p-Cresol												
37.34	0.041	y				34.7	3.50	35.8	3.37			
46.86	0.184	x				44.6	3.85					
54.13	0.805	y										
54.72	1.066	x										
m-Cresol												
37.84	0.011	+36°				36.8	3.22	36.2	3.34	46.4	shoulder	<3.90
46.91	0.120	− 6°				45.5	3.73			51.8	47—58→	4.78
53.38	0.914	+90°										
54.05	1.057	+ 3°										
o-Cresol												
37.73	0.015	−32°				36.5	3.41	36.4	3.32	47.0	shoulder	3.78
46.73	0.116	+16°				46.3	3.79			52.2	48—57→	4.85
53.23	0.923	−79°										
54.29	1.051	+ 8°										

[a] Data used for parameter determination.

Table 10. Calculated and observed electronic transitions of naphthols. Transition frequencies in kK.

Molecule	Calculation			Observation Baba and Suzuki [25] isooctane		
	ν	f	pol	ν_{max}	range	f
α-Naphthol	33.03	0.005	−25°	31.10	30.5−31.5	0.016
	36.44	0.289	+84°	34.57	31.5−40	0.102
	45.19	0.040	+ 4°			
	46.15	0.219	− 4°	43.57	41.5−44.5	0.328
	48.33	0.086	+11°			
	49.17	1.576	− 1°	46.82	44.5−50.5→	0.892
	53.45	0.702	+90°			
	56.49	0.030	+86°			
	58.73	0.109	−27°			
β-Naphthol	32.69	0.017	−49°	30.47	30 −34	0.021
	37.49	0.197	−76°	36.60	34 −40	0.081
	45.26	0.251	+ 7°			
	47.11	0.640	+21°	44.58	41 −50.5→	1.06
	48.36	0.935	+ 7°			
	49.73	0.155	+18°			
	51.51	0.721	−63°			
	56.02	0.099	−19°			
	59.01	0.063	−84°			

Table 11. Calculated and observed electronic transitions of benzofuran. Transition frequencies in kK.

Calculations			Observation Klevens and Platt [24] heptane		
ν	f	pol	ν_{max}	range	log ε
36.72	0.020	−86°	⎧35.5⎫ ⎩36.6⎭	35−38	⎧3.32⎫ ⎩3.38⎭
42.03	0.260	−31°	41.3	38−45	4.00
47.95	0.580	+29°			
49.55	0.190	−86°			
53.39	0.943	−16°	50.0	45−58→	4.49
55.17	0.201	+85°			
56.48	0.067	−13°			
60.50	0.412	+79°			
63.76	0.052	+51°			
66.21	0.194	−74°			
66.78	0.083	−90°			

in β-naphthol. The broad experimental peaks in the region 40—50 kK make it impossible to say anything definite about the higher transitions, but the calculated values look very reasonable compared to the experimental curves. The shift of the whole energy scale from experiment to calculation (calculated values 1—2 kK higher) could be partly due to solvent effects. If the first

Table 12. Calculated and observed electronic transitions of furan and methylfurans. Transition frequencies in kK.

Molecule	Calculation			Observation Pickett [17,18] vapour		
	ν	f	pol	ν_{max}	range	log ε
Furan	45.68	0.294	x	46 shoulder		2.9
	48.44	0.117	y	48.9 [a]	46—52	3.6
				52.2	52—58	4.1
	59.81	0.821	y	59.6 [a]	59—61.5	3.8
	62.51	0.217	x	62.8 [a]		
2-Methylfuran	44.62	0.307	− 4°			
	49.04	0.080	+71°			
	59.12	0.866	−87°			
	63.01	0.216	+ 8°			
3-Methylfuran	44.64	0.260	−19°			
	48.14	0.178	+58°			
	59.58	0.783	+82°			
	62.51	0.254	−26°			
2,5-Dimethylfuran	44.08	0.331	x			
	49.14	0.035	y			
	58.69	0.919	y			
	63.46	0.208	x			
2,3-Dimethylfuran	43.25	0.279	−14°			
	48.95	0.132	+57°			
	58.89	0.856	+87°			
	62.98	0.227	−10°			

[a] Data used for parameter determination.

two narrow peaks in the benzofuran curve are interpreted as vibrational peaks belonging to the same electronic transition the agreement is satisfactory between the calculated and observed benzofuran spectra. In the methylfurans it is seen that the substituent effect on the spectra is small. It was already seen in the cresols that the influence of the methyl group was small.

Bearing in mind what was already said about calculated and experimental spectra in section 6, one sees that the calculations give quite good results on the whole in the molecules, which have been considered in this paper.

8. OTHER CALCULATIONS ON MOLECULES CONTAINING OXYGEN

Quite a few calculations on oxygen-containing molecules have been published; cf., e.g., Refs. 21, 25, 27, 31—39. Of these investigations Nos. 31—34 are particularly interesting to compare to the present paper, since a large number of molecules are considered in them.

Pukanic *et al.*[31] have used the modification of the PPP method proposed by Adams and Miller [40] on phenol, dihydroxybenzenes and naphthols. Though

their results are reasonable, the method seems to be unpractical to use on a large scale since new empirical parameters must be introduced for every new molecule.

Flurry et al.[32] have included two-center core integrals between non-neighbours, while the other integrals are treated in the usual way. This means, however, that the different types of integrals are not approximated in a consistent manner.[7] They have calculated IP's, electronic transitions, and charge densities on several oxygen- and nitrogen-containing molecules. The oxygen parameters have been fitted to the furan spectrum, but they quote only one experimental value, 48.8 kK. Their charge densities in furan come out opposite to what one would expect from chemical considerations. Their results for those mole-cules, which are also treated in this paper, are collected in Table 13.

Table 13. Results obtained by Flurry et al.[32] with their best parameter set.

Molecule	IP (eV)	Singlet-singlet transition energies (kK)		
Furan	8.93	48.7	49.4	67.6
Benzofuran	8.69	37.3	42.5	49.0
Phenol	9.37	39.1	48.8	56.2
Resorcinol	8.61	37.1	46.2	53.2

	π-Electron densities								
	1	2	3	4	5	6	7	8	9
Furan	1.768	1.049	1.067						
Benzofuran [a]	1.799	1.017	1.086	1.009	1.025	1.013	1.048	1.014	0.989

[a] Renumbered to be the same as in the present paper.

There it is seen, that the IP and the transition energies for phenol are too high. The adiabatic and vertical IP's of phenol are 8.46 eV [14] and 8.75 eV.[15] The singlet-singlet transitions are about 2 kK too high. These values are a good illustration of a big problem in semi-empirical calculations on oxygen-containing molecules.

Many workers have used furan to determine the oxygen parameters, but there are just about as many interpretations of the furan spectrum as there are calculations on furan. Thus, it can be difficult to see whether poor results on other molecules are due to inconsistencies in the method or incorrect assumptions about the furan spectrum.

Billingsley and Bloor [33] have used a simple PPP—SCF method in which parameter variation with charge densities and bond orders is neglected. They have tried to find a parameter set to treat polysubstituted benzenes and five-membered ring heterocyclics containing nitrogen, oxygen, and sulfur. They only report calculated IP's and singlet-singlet transitions. Their calculated IP's are compared to estimated charge-transfer data. The values obtained in this way are less accurate and found to be too high for molecules

for which there are good direct measurements of IP's for comparison. It should be noted that the *W* parameter is sensitive to the assumed IP value. The oxygen-containing molecules are furan, benzofuran, and dibenzofuran. The results are reproduced in Table 14. The previously mentioned problem

Table 14. Results obtained by Billingsley and Bloor.[33] The experimental data reported by them is included for comparison.

| Molecule | IP (eV) | | Electronic transition energies (kK) | | | |
| | Calc. | Estimated from charge-transfer data | Calc. | | Exptl. | |
			ν	f	ν	$\log \varepsilon$
Furan	9.73	9.77	46.31	0.31	46.41	3.7
			48.09	0.02		
Benzofuran	9.41	9.66	36.29	0.006	35.59	3.5
			41.14	0.39	40.90	4.0
			47.39	0.72	48.54	4.4
			50.39	0.09		
			52.42	0.52		

[a] Data used for parameter determination.

with the furan spectrum is noted in this table, too. Neither bond orders nor π-electron densities are reported. Thus, it is hard to get an idea of how reliable their method is.

Nishimoto and Forster [34] have done extensive calculations on nitrogen and oxygen-containing molecules. They use a variable β-method. The two-center core integral β between nearest neighbours is calculated from the formula

$$\beta = Ap + B$$

where p is the bond order. The constants A and B depend on the type of bond. But B is also dependent on the size of the molecule (number of rings). The calculations are repeated until self consistency is obtained in β. But the electronic repulsion integrals γ are calculated from an assumed fixed geometry, although rather large deviations from the assumed regular hexagons occur in, *e.g.*, the naphthols.

Their obtained values seem to be satisfactory, though the IP's are somewhat low.

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