

Semi-empirical Parameters in π -Electron Systems

III. Heteroatomic Molecules Containing Nitrogen

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A modification of the Pariser-Parr-Pople method has been extended to azines and to unsaturated amines. The method has been applied in calculations of bond lengths, ionization potentials and electronic transitions of both $\pi-\pi^*$ and $n-\pi^*$ types. The overall agreement between calculated values and measurements is satisfactory.

I. INTRODUCTION AND SUMMARY

The Pariser-Parr-Pople method has been widely used in calculations on π -electron systems, commonly with considerable success. Several schemes have been suggested for the evaluation of the semi-empirical parameters of this method. In previous papers of the present series^{1,2} such a scheme was suggested by Roos and Skancke and applied to unsaturated pure hydrocarbons and to methyl substituted hydrocarbons. The present investigation is an extension of this scheme to nitrogen containing molecules. Preliminary results of this extension have been published earlier.³ According to the adopted method as many as possible of the necessary parameters are to be determined from experimental data of a chosen set of small standard molecules. A special feature of the method is that a certain delocalization of the one-electron, "one-centre" parameter W_μ is included by introduction of corrections depending on bond distances and kind of bonded atoms.

The semi-empirical method and the scheme for parameter evaluation are briefly described in Section II. Section III deals with the explicit determination of the parameters. For nitrogen contributing one π -electron and a σ lone pair the following set of standard molecules have been used: pyridine, pyrimidine, and pyrazine. Pyrrole and aniline have been chosen as standards for nitrogen contributing a π lone pair. The finally adopted parameter values are collected in Table 1. These values have then been applied in calculations of ground state properties and singlet transition energies of some nitrogen-containing test molecules: *sym*-triazine, quinoline, isoquinoline, *aza*-azulene, acridine, phenylenediamines, *sym*-benzenetriamine, indole, and carbazole.

Table 1. Semi-empirical parameters for heteroatomic molecules containing nitrogen.

Carbon ² π -parameters $R_{CC}^\circ = 1.397 \text{ \AA}$		Nitrogen (present work) $R_{CN}^\circ = 1.338 \text{ \AA}$				
		Pyridine-nitrogen π -parameters	Pyrrole-nitrogen π -parameters	Pyridine-nitrogen σ -parameters		
$\gamma_{\pi\pi}$	11.97 eV	$\gamma_{\pi\pi}$	15.44 eV	15.44 eV	$\gamma_{\sigma\sigma}$	17.53 eV
γ_{CC}°	6.91 eV	γ_{CN}°	7.16 eV	6.34 eV	$\gamma_{\sigma\pi}$	13.95 eV
δ_{CC}^γ	-3.99 eV/Å	δ_{CN}^γ	-3.99 eV/Å	-3.99 eV/Å	$K_{\sigma\pi}$	1.57 eV
β_{CC}°	-2.42 eV	β_{CN}°	-2.72 eV	-2.25 eV	W_σ	-10.96 eV
δ_{CC}^β	3.05 eV/Å	δ_{CN}^β	2.6 eV/Å	2.6 eV/Å	$\gamma_{\sigma 1\pi 2}$	7.33 eV
W_C°	-9.84 eV	W_N°	-12.57 eV	-8.52 eV		
ΔW_C°	0.07 eV	$\Delta W_N^\circ(C)$	0.14 eV	0.14 eV		
δ_{CC}^W	9.22 eV/Å	$\Delta W_C^\circ(N)$	0.03 eV	0.03 eV		
		δ_{CN}^W	5.6 eV/Å	5.6 eV/Å		

For comparison also the hydrocarbons azulene, anthracene, and phenanthrene have been studied.

The results of the investigation are presented and discussed in Section IV. They are compared to experiments when available. It is found that the overall agreement between theory and observations is quite satisfactory. This is rather gratifying since the present study is part of a research project aiming at a theoretical investigation of biologically important molecules. In fact, calculations on porphyrin compounds with promising preliminary results are in progress in this laboratory.

II. METHOD

The Pariser-Parr-Pople (PPP) method in the SCF-MO-LCAO form has been adopted. The assumption of zero differential overlap (ZDO) made in the PPP method can be summarized as follows:

$$S_{\mu\nu} = (\mu|S|\nu) = \delta_{\mu\nu} \quad (1)$$

$$\alpha_\mu = (\mu|H^{\text{core}}|\mu) \neq 0 \quad (2)$$

$$\beta_{\mu\nu} = (\mu|H^{\text{core}}|\nu) \neq 0 \quad \text{when } \mu \text{ and } \nu \text{ are neighbours} \quad (3)$$

$$\beta_{\mu\nu} = (\mu|H^{\text{core}}|\nu) = 0 \quad \text{when } \mu \text{ and } \nu \text{ are non-neighbours} \quad (4)$$

$$(a\beta|1/r_{12}|\mu\nu) = \delta_{a\mu} \delta_{\beta\nu} \gamma_{\mu\nu} \quad (5)$$

In a previous paper one of us⁴ has examined the grounds for the ZDO-approximation and showed that it can be described as a second order theory in the overlap integral, $S_{\mu\nu}$, between neighbouring AO's. The eqns. (1)–(5) must then be interpreted as given in an orthogonalized atomic orbital (OAO) basis. The resonance integral, $\beta_{\mu\nu}$, and the Coulomb integral, $\gamma_{\mu\nu}$, were shown to be transferable from one molecule to another, *i.e.* the contributions from other centres than μ and ν are of third order in $S_{\mu\nu}$. The core integral, α_μ ,

is non-local, but can be expressed in terms of the $\gamma_{\mu\nu}$'s and a parameter W_μ , first introduced by Goeppert-Mayer and Sklar:⁵

$$W_\mu = \alpha_\mu + (n_\mu - 1)\gamma_{\mu\mu} + \sum_{\nu \neq \mu} n_\nu \gamma_{\mu\nu} \quad (6)$$

where n_μ is the number of electrons contributed by the AO μ . W_μ is local to the first order in the overlap integral only. The second order terms include contributions from the nearest neighbours.⁴

In the present investigation the semi-empirical parameters W_μ , $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ for nearest neighbours have been chosen according to the scheme mentioned above. The parameters have been determined from experimental data of a chosen set of small standard molecules. The SCF-MO's have been evaluated by means of a data machine programme written by P. Eisenberger, T. Alm and B. Roos. This programme also calculates the energy levels of excited states by mixing all configurations obtained from single excitations. Oscillator strengths for the dipole transitions and eigenvectors for the multi-configurational problem are also obtained directly from the computer. The CDC 3600 machine at the University of Uppsala has been used for the present calculations.

III. SEMIEMPIRICAL PARAMETERS

A. Carbon parameters

The carbon parameters for unsaturated pure hydrocarbons have been published previously by Roos and Skancke,¹ *cf.* also Ref. 3.

The different parameters are assumed to be linear functions of the inter-nuclear distance, $R_{\mu\nu}$. This assumption seems to be reasonable because of the narrow range of bond length variations.

For an sp^2 hybridized carbon atom the core integral W_C can be written:

$$W_C(P, Q, T) = W_C^\circ + \Delta W_C(P) + \Delta W_C(Q) + \Delta W_C(T) \quad (7)$$

where P, Q, and T are the atoms bounded to C. $\Delta W_C(Q)$ is the correction due to the replacement of a hydrogen atom by the atom (or saturated radical) Q. This correction is assumed to depend on the distance as follows:

$$\Delta W_C(Q) = \Delta W_C^\circ(Q) + \delta_{CQ}^W (R_{CQ} - R_{CQ}^\circ) \quad (8)$$

where R_{CQ}° is a suitably chosen standard length of the CQ bond.

The resonance integral, $\beta_{\mu\nu}$, and the Coulomb integral, $\gamma_{\mu\nu}$, between nearest neighbours contribute two parameters each:

$$\beta_{\mu\nu} = \beta_{\mu\nu}^\circ + \delta_{\mu\nu}^\beta (R_{\mu\nu} - R_{CC}^\circ) \quad (9)$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^\circ + \delta_{\mu\nu}^\gamma (R_{\mu\nu} - R_{CC}^\circ) \quad (10)$$

R_{CC}° has been chosen to be equal to the nearest neighbour distance in the benzene molecule (1.397 Å).

The one-centre integral, $\gamma_{\mu\mu}$, has been obtained from spectral data.⁶

The ball approximation has been used for the $\gamma_{\mu\nu}$'s between non-neighbours. The previously published set of carbon parameters² is reproduced in Table 1.

B. Parameters for nitrogen, contributing one π -electron

In the case of heteroatoms the experimental information is not as complete and accurate as for pure hydrocarbons. Therefore we cannot expect to be able to determine all parameters for nitrogen with the same accuracy as in the case of carbon.

For pyridine nitrogen, we have chosen pyridine, pyrimidine and pyrazine as standard molecules. The geometry of pyridine has been very accurately determined by Bak *et al.*⁷ from microwave spectroscopy. Their data have been used in the present investigation. The geometry of pyrimidine and pyrazine is known from X-ray investigations of the crystalline state by Wheatley.⁸ These data have been used as initial values in a theoretical self-consistent determination of the geometry from the following bond order—bond length relations:⁹

$$R_{\mu\nu}(\text{CC}) = 1.517 - 0.180 p_{\mu\nu} \quad (11)$$

$$R_{\mu\nu}(\text{CN}) = 1.458 - 0.180 p_{\mu\nu} \quad (12)$$

where $R_{\mu\nu}$ is the interatomic distance and $p_{\mu\nu}$ the corresponding bond order. It is assumed that the difference between double and single bond lengths is 0.18 Å for $\text{C}(sp^2)\text{—N}(sp^2)$ as well as for CC bonds. In (12) the values of *sym*-triazine ($p = 2/3$, $R(\text{CN}) = 1.338$ Å¹⁰) have been used.

The number of parameters to be determined are nine, namely W_N° , $\Delta W_C^\circ(\text{N})$, $\Delta W_N^\circ(\text{C})$, δ_{CN}^W , β_{CN}° , δ_{CN}^β , γ_{CN}° , $\delta_{\text{CN}}^\gamma$ and $\gamma_{\mu\mu}$. In order to limit this number, the parameters δ_{CN}^W , δ_{CN}^β , $\delta_{\text{CN}}^\gamma$ and $\Delta W_N^\circ(\text{C})$ * have been estimated by means of the corresponding carbon parameters. As mentioned above, $\gamma_{\mu\mu}$ has been obtained from atomic spectral data.

The remaining four parameters, W_N° , $\Delta W_C^\circ(\text{N})$, β_{CN}° , and γ_{CN}° have been determined through a least squares fit to the following twelve experimental data: the vertical ionization potentials (IP) and the three lowest singlet $\pi\text{—}\pi^*$ transitions (vapour phase) of all three standard molecules. The optimal choice of the set of four parameters leads to very satisfactory agreement between calculated and experimental values of most of the twelve observable

Table 2. Calculated ionization potentials of the standard molecules compared to the observed values, used for parameter determination. All values in eV.

Molecule	IP (calc.)	IP (obs.) ²⁰
Pyridine (π)	9.27	9.28
Pyrimidine	9.50	9.47
Pyrazine	9.32	9.27
Pyridine (σ)	10.5	10.54
Pyrrole	8.23	8.22
Aniline	7.66	7.71

* Cf. Ref. 4b, Table II and eqn. (32).

Table 3. Calculated and observed electronic transitions of the standard molecules. Transition frequencies in kK.

Molecule	Calculation		Observations					
	ν	f	Vapour			Solution		
			ν_{\max}^a	range ^b	f^c	ν_{\max}	range	f
Pyridine (π)	40.60	0.008	Pickett <i>et al.</i> ¹⁵			Favini and Bellobono ⁴⁹		
	52.02	0.16	40.1*	36-48	0.04	39.8	38-42	0.04
	57.45	1.16	51.4*	48-54	0.10	50.6	48-53	0.10
	59.24	0.98	57.5*	54-64	1.3	56.2	53-58	0.66
Pyrimidine	42.14	0.01	Parkin and Innes ⁵⁰			40.9	40-44	0.025
	54.08	0.30	42.5*	39-47	0.05	53.3	50-55	0.13
	60.17	1.11	54.2*	52-55	0.16	~58	55-58→	~0.43
	61.60	0.86	~60*	58-64	vs	~62	58-64	
Pyrazine	42.01	0.03	39.8*	37-46	0.10	38.3	37-40	0.085
	52.30	0.35	53.2*	50-54	0.145	51.5	50-55	0.12
	59.19	1.10	61.9*	60-65	vs			
	66.27	0.89						
Pyridine (σ)	37.0	0.01 ^d	Refs. 21, 22, 23					
	49.3	0	~37.0					
Pyrrole	47.32	0.32	Pickett <i>et al.</i> ¹⁵			Klevens and Platt ¹⁶		
	49.11	0.06	47.4*	46-49	>0.12	47.8	43-52	
	58.98	0.90	54.7	54-57	>0.08	48.9		
	62.89	0.31	58.5	57-59	>0.60		53-58→	
Aniline	36.07	0.054	Kimura <i>et al.</i> ³⁰					
	44.10	0.29	35.5*	34-37	0.028			
	51.33	0.38	43.5*	41-47	0.14			
	54.35	0.92	51.6	48-59	0.51			
	59.99	0.69	55.5	48-59	0.57			
	61.71	0.11	63.5 ^e	59-66	(0.68)			

* Data used for parameter determination.

^a s shoulder. ^b An arrow after the last value indicates a cut-off in the measurements. ^c vs very strong, m medium, w weak.

^d All transition moment integrals except $\int s(N)z p_z(N) d\tau$ are neglected, *cf.* Goodman.⁴⁸

^e Two bands.

as is shown in Tables 2 and 3. Only the calculated splitting of the two B_{3u} states of pyrazine is somewhat too small. All the calculated oscillator strengths are also in good agreement with the observations; *cf.* Table 3.

The experimental geometry is very well reproduced in the case of pyridine, as can be seen from Table 4. For pyrimidine and pyrazine there are minor

differences between theory and experiment. These differences are, however, of the same order as the experimental accuracy.

The adopted parameter set is listed in Table 1.

An attempt has been made to include the method of variable electronegativity¹¹ in the present computational scheme. Since most of the parameters of the heteroatom are determined from molecular measurements, the effect of a typical charge on this atom is already included to a great extent. Consideration of the variable electronegativity for the remaining parameters did not change the calculated data enough to distinguish them from the values of Tables 2 and 3. This result is not unexpected, since the changes of W_μ and of $\gamma_{\mu\mu}$ due to the variable electronegativity method give opposing contributions to the Fock operator. Therefore we do not find it justified to include this refinement in our scheme.

C. Parameters for nitrogen, contributing a π lone pair

In this case, pyrrole and aniline have been chosen as standard molecules. The geometry of pyrrole has been very accurately determined by Bak *et al.*¹² from microwave spectroscopy. The aniline geometry is still an unsettled problem. Recent microwave studies by Lister and Tyler¹³ show that the plane of the HNH-radical forms an angle of 39.35° with the plane of C_6H_5N . Further, the angle HNH was found to be 113.9° and the CN distance to be 1.431 Å. The distance R_{CN} in the anilinium ion has been determined previously by Abrahams and Robertson¹⁴ to be 1.36 Å in the solid state. Fortunately our parameter set is found to be rather insensitive to the detailed choice of the value of R_{CN} . We have chosen a value intermediate between the different experimental findings, *i.e.* $R_{CN} = 1.385$ Å, as initial bond distance. Furthermore, we have assumed the molecule to be planar with the benzene geometry of the carbon ring. A consideration of the nonplanarity would only slightly modify the obtained parameter values.

Alternative choices of standard molecules can be discussed. As an example, divinylamine ought to be a suitable standard molecule. Unfortunately, complete and accurate experimental information about this molecule, necessary for our purpose, is still lacking.

The π lone pair parameters W_N° , β_{CN}° and γ_{CN}° have been determined from pyrrole- and aniline-data. The remaining parameters have been assumed to be the same as in the case of pyridine-nitrogen.

The following data have been used for the parameter determination: the first vertical IP of aniline and pyrrole, the lowest singlet transition (vapour phase) of pyrrole, and the two lowest singlet transitions (vapour phase) of aniline. Since five observations have been used to evaluate three parameters, the values have been determined by a least squares fit.

The optimal choice of W_N° , β_{CN}° , and γ_{CN}° leads to calculated values of the different observables, as shown in Tables 2 and 3, in satisfactory agreement with experiments. It is not possible to find any reasonable set of parameters which reproduces the second band system of pyrrole observed by Pickett

*et al.*¹⁵ This second weak transition cannot be traced in the solution spectra published by Klevens and Platt¹⁶ (Table 3). Therefore we suggest that this band system might be due to a Rydberg transition. The same conclusion was reached by one of us⁹ from a previous calculation on pyrrole with a different choice of parameters.

Several semi-empirical calculations for pyrrole have been published previously. Chiorboli *et al.*¹⁷ and Julg and Carles¹⁸ conclude that the second band system in pyrrole can be assigned to a $\pi-\pi^*$ transition, only if mixing of the singly excited configurations is rejected. We cannot see any reason why pyrrole should be given a different theoretical treatment from other molecules. Therefore, we prefer to consider the assignment of the second band system in pyrrole as an open question. A similar conclusion is reached by Berthod *et al.*¹⁹ Further experimental information may settle the problem.

The adopted parameter set is given in Table 1.

D. Parameters of one sigma lone pair

The sigma lone pair on nitrogen, σ , has been treated as an sp^2 -hybrid, *e.g.*

$$\sigma = \frac{1}{\sqrt{3}} (s + \sqrt{2} p) \quad (13)$$

The one-centre two-electron integrals, $\gamma_{\sigma\sigma}$, $\gamma_{\sigma\pi}$, and $K_{\sigma\pi}$ (the exchange integral) have been determined from atomic spectral data. In the calculation of non-neighbour $\gamma_{\sigma\sigma}$'s the orbital σ has been replaced by a uniformly charged sphere with its origin in the centre of gravity of charge of the sp^2 -hybrid.

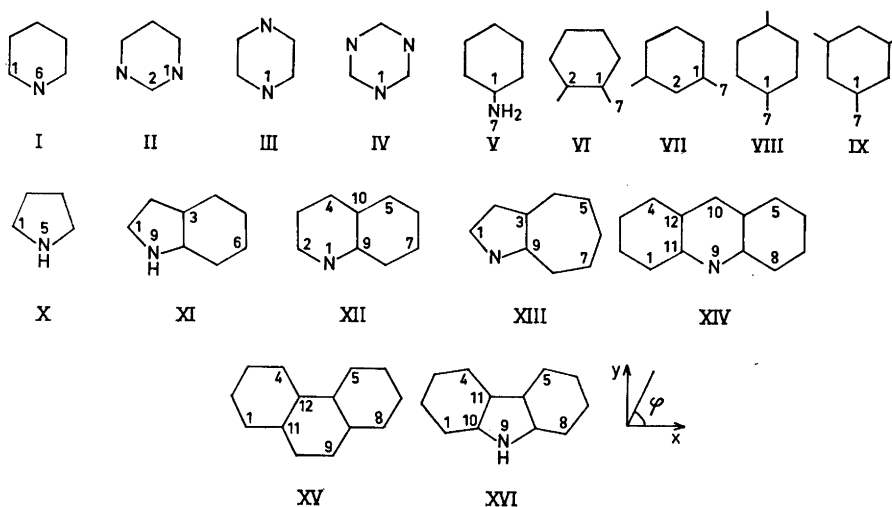


Fig. 1. I: Pyridine, II: Pyrimidine, III: Pyrazine, IV: *sym*-Triazine, V: Aniline, VI: *o*-Phenylenediamine, VII: *m*-Phenylenediamine, VIII: *p*-Phenylenediamine, IX: *sym*-Benzenetriamine, X: Pyrrole, XI: Indole, XII: Quinoline, XIII: 10-Aza-azulene, XIV: Acridine XV: Phenanthrene, XVI: Carbazole.

Table 4. Calculated and observed bond distances. All values in Å. The numbering of the atoms is given in Fig.1.

Molecule	Bond	Bond order	Bond length		
			Calc. present work	Calc.	Obs.
Pyridine	2-1	0.6558	1.3990	1.398 ⁵¹	1.3958 ⁷
	3-2	0.6722	1.3960	1.397	1.3936
	6-1	0.6694	1.3375	1.334	1.3394
Pyrimidine	2-1	0.660	1.339		1.33, 1.34 ⁸
	4-3	0.675	1.337		1.35, 1.36
	5-4	0.661	1.398		1.38, 1.41
Pyrazine	2-1	0.675	1.337		1.334 ⁸ 1.341 ³⁶
	3-2	0.645	1.401		1.378 1.395
<i>sym</i> -Triazine	2-1	0.647	1.342	1.334 ⁵¹	1.338 ¹⁰
Pyrrole	2-1	0.790	1.375	1.37 ¹⁷	1.381 ¹²
	3-2	0.541	1.420	1.43	1.417
	5-1	0.472	1.373	1.37	1.374
Aniline	2-1	0.623	1.405	1.406 ^a	1.397 ^b
	3-2	0.673	1.396	1.395	1.397
	4-3	0.662	1.398	1.397	1.397
	7-1	0.355	1.394	1.390	1.36 ¹⁴ -1.43 ¹³
<i>o</i> -Phenylene-diamine	2-1	0.592	1.411	1.413 ²⁷	
	3-2	0.644	1.401	1.403	
	4-3	0.658	1.399	1.397	
	5-4	0.669	1.397	1.398	
	7-1	0.320	1.401	1.395	
<i>m</i> -Phenylene-diamine	2-1	0.629	1.404	1.404 ²⁷	
	4-3	0.617	1.406	1.407	
	5-4	0.670	1.397	1.396	
	7-1	0.358	1.394	1.391	
<i>p</i> -Phenylene-diamine	2-1	0.626	1.404	1.406 ²⁷	
	3-2	0.671	1.396	1.395	
	7-1	0.334	1.398	1.394	
<i>sym</i> -Benzene-triamine	2-1	0.624	1.405		
	7-1	0.359	1.393		
Quinoline	2-1	0.758	1.322	1.319 ⁵¹	
	3-2	0.551	1.418	1.416	
	4-3	0.767	1.379	1.380	
	6-5	0.773	1.378	1.380	
	7-6	0.547	1.419	1.415	
	8-7	0.776	1.377	1.380	
	9-1	0.540	1.361	1.358	
	9-8	0.499	1.427	1.424	

Table 4. Continued 2.

Isoquinoline	10-4	0.527	1.422	1.422	
	10-5	0.509	1.425	1.423	
	10-9	0.567	1.415	1.415	
	2-1	0.758	1.322	1.319 ⁶¹	
	3-2	0.574	1.355	1.350	
	4-3	0.751	1.382	1.382	
	6-5	0.767	1.379	1.381	
	7-6	0.557	1.417	1.414	
	8-7	0.766	1.379	1.381	
	9-1	0.513	1.425	1.423	
	9-8	0.517	1.424	1.422	
	10-4	0.527	1.422	1.422	
	10-5	0.514	1.425	1.423	
10-9	0.576	1.413	1.415		
Azulene	2-1	0.662	1.398		1.394 ⁶⁹ 1.399 ⁷⁰
	3-2	0.600	1.409		1.398 1.418
	4-3	0.629	1.404		1.391 1.383
	5-4	0.646	1.401		1.400 1.406
	6-5	0.653	1.399		1.392 1.403
	9-3	0.247	1.473		1.498 1.501
10-Aza- azulene	2-1	0.612	1.407		
	3-2	0.651	1.400		
	4-3	0.579	1.413		
	5-4	0.678	1.395		
	6-5	0.634	1.403		
	7-6	0.662	1.398		
	8-7	0.640	1.402		
	9-3	0.273	1.468		
	9-8	0.631	1.403		
	10-1	0.693	1.333		
10-9	0.586	1.353			
Indole	2-1	0.834	1.367	1.351-1.356 ⁸²	
	3-2	0.435	1.439	1.456-1.451	
	4-3	0.573	1.414	1.409-1.419	
	5-4	0.726	1.386	1.389-1.379	
	6-5	0.604	1.408	1.404-1.415	
	7-6	0.722	1.387	1.390-1.380	
	8-7	0.577	1.413	1.405-1.418	
	8-3	0.597	1.410	1.400-1.394	
	9-8	0.432	1.380	1.407-1.390	
	9-1	0.404	1.385	1.404-1.388	
Carbazole	2-1	0.704	1.390	1.394-1.388 ⁸²	
	3-2	0.624	1.405	1.400-1.406	
	4-3	0.704	1.390	1.393-1.387	
	10-1	0.598	1.409	1.400-1.408	
	10-9	0.377	1.390	1.415-1.402	
	11-4	0.604	1.408	1.404-1.410	
	11-10	0.602	1.409	1.400-1.397	
	13-11	0.364	1.452	1.464-1.463	

Table 4. Continued 3.

Phenanthrene	2-1	0.739	1.385	1.386 ²⁵	1.381 ³³
	3-2	0.589	1.410	1.408	1.398
	4-3	0.736	1.386	1.387	1.383
	10-9	0.829	1.367	1.367	1.372
	11-1	0.554	1.416	1.414	1.457
	11-10	0.443	1.438	1.438	1.390
	12-4	0.562	1.417	1.413	1.405
	12-11	0.604	1.408	1.410	1.404
	14-12	0.410	1.443	1.444	1.448
	Anthracene	2-1	0.801	1.373	
3-2		0.511	1.425		1.419
11-1		0.464	1.433		1.436
11-9		0.622	1.405		1.399
12-11		0.521	1.423		1.428
Acridine	2-1	0.809	1.371	1.376 ⁵¹	1.375 ⁶⁸
	3-2	0.496	1.428	1.421	1.438
	4-3	0.810	1.371	1.376	1.356
	11-1	0.456	1.435	1.431	1.430
	11-9	0.605	1.349	1.341	1.345
	12-4	0.455	1.435	1.430	1.435
	12-10	0.632	1.403	1.406	1.375
	12-11	0.508	1.426	1.424	1.435

^a Calculated from bond orders published by Kwiatkowsky³¹ and the present eqns. (11) and (12). ^b The benzene value.

W_{σ} and $\gamma_{\sigma 1, \pi 2}$, where 1 and 2 are neighbours, have been determined from the lone pair ionization potential²⁰ and the lowest $n-\pi^*$ transition²¹⁻²³ of pyridine.

The obtained parameter values are found in Table 1.

IV. RESULTS AND DISCUSSION

The parameter sets, listed in Table 1, have been applied in investigations of some test molecules containing nitrogen atoms. For comparison calculations on some pure hydrocarbons have also been performed. Bond lengths, net charges, vertical ionization potentials, dipole moments, and electronic spectra are reproduced in Tables 4-20. The numbering of atoms and choice of axes are given in Fig. 1.

1. *Bond lengths and π -electron densities.* The bond order-bond length relations (11) and (12) have been applied. For those molecules where the bond distances, $R_{\mu\nu}$, calculated in the first cycle, deviated substantially from the assumed ones, the calculation was repeated with the obtained values of $R_{\mu\nu}$ as input. This procedure was continued until self-consistency was achieved. The results of the bond length calculations are collected in Table 4, where also experimental data and the results of other recent theoretical investigations

Table 5. π -Electron densities. The numbering of the atoms is given in Fig. 1.

Molecule	Atom No.	π -electron density	Molecule	Atom No.	π -electron density
Pyridine	1	0.970	Carbazole	1	1.077
	2	0.999		2	1.003
	3	0.992		3	1.029
	6	1.070		4	1.012
Pyrimidine	1	1.069		9	1.751
	2	0.944		10	0.989
	4	0.960	11	1.014	
	5	0.998	Phenanthrene	1	1.011
Pyrazine	1	1.062		2	1.014
	2	0.969		3	1.007
<i>sym</i> -Triazine	1	1.253		4	1.022
	2	0.747		9	1.017
Pyrrole	1	1.072		11	0.966
	2	1.099	12	0.963	
	5	1.656	Quinoline	1	1.094
Aniline	1	0.950		2	0.963
	2	1.078		3	1.013
	3	0.990		4	1.002
	4	1.035		5	1.017
	7	1.878		6	1.008
<i>o</i> -Phenylene-diamine	1	1.013		7	1.012
	3	1.068		8	1.002
	4	1.023		9	0.949
	7	1.895		10	0.941
<i>m</i> -Phenylene-diamine	1	0.942	Isoquinoline	1	0.967
	2	1.158		2	1.079
	4	1.111		3	0.997
	5	0.981		4	1.009
	7	1.877		5	1.011
<i>p</i> -Phenylene-diamine	1	0.979		6	1.007
	2	1.066		7	1.008
	7	1.889		8	1.013
<i>sym</i> -Benzene-triamine	1	0.934		9	0.957
	2	1.188		10	0.951
	7	1.877	Azulene	1	1.007
Indole	1	1.064		2	1.129
	2	1.106		3	0.915
	3	1.006		4	0.956
	4	1.006		5	1.007
	5	1.032		6	0.979
	6	1.008	10-Aza-azulene	1	0.948
	7	1.079		2	1.170
	8	0.992		3	0.963
	9	1.706		4	0.916
		5		1.010	
		6		0.949	
		7		0.985	
		8		0.959	
		9		0.941	
		10		1.158	

Table 5. Continued.

Molecule	Atom No.	π -electron density
Anthracene	1	1.003
	2	1.017
	9	1.053
	11	0.954
Acridine	1	0.996
	2	0.989
	3	1.010
	4	1.018
	9	1.311
	10	1.032
	11	0.856
	12	0.959

are given. On the whole there is a good agreement between the present results and experimental data. Yet great discrepancies are found for phenanthrene, a result also obtained by Skancke²⁴ and Nishimoto.²⁵ The results of the various theoretical determinations are very close to each other. It can therefore be concluded that calculated bond lengths are rather insensitive to the choice of semi-empirical parameters, which may indicate the possibility of predicting bond lengths from PPP-calculations.

The obtained π -electron densities are given in Table 5.

2. *Vertical ionization potentials.* The molecular vertical IP's have been calculated by Koopmans' theorem. The agreement between calculated and observed values of the first IP's (Tables 6 and 7) is in general very good. In Table 7 the IP of aniline is compared with the IP's of the phenylenediamines and of *sym*-benzenetriamine and the differences, Δ IP, are quoted. The calculated values of Δ IP for *o*-, *m*- and *p*-phenylenediamine have the same relative order of

Table 6. Calculated and observed ionization potentials of test molecules. Values given in eV.

Molecule	IP (calc.)	IP (obs.)			
<i>sym</i> -Triazine	11.21				
Quinoline	8.27				
Isoquinoline	8.21				
Indole	7.86				
Carbazole	7.68				
Phenanthrene	7.93	8.03 ⁵⁴			
Azulene	7.30	7.41 ⁵³			
10-Aza-azulene	7.75				
Anthracene	7.51	7.55 ⁵⁴	7.85 ⁵⁵	7.15 ⁶⁴	7.38 ⁶⁵
Acridine	8.07				

Table 7. Calculated and observed ionization potentials. Values given in eV.

Molecule	Theoretical				Experimental				
	Present work		Kwiatkowski ²⁷		Turner ²⁰	Briegleb and Czekalla ³⁵		Farrell and Newton ^{26,37}	
	IP	Δ IP	IP	Δ IP	IP	IP	Δ IP	IP	Δ IP
Aniline	7.66	—	9.04	—	7.71	7.85–7.95		7.76	—
<i>o</i> -Phenylenediamine	7.03	0.63	8.46	0.58	—	7.45	0.4–0.5	7.35	0.41
<i>m</i> -Phenylenediamine	7.20	0.46	8.67	0.37	—	—	—	7.48	0.28
<i>p</i> -Phenylenediamine	6.80	0.86	8.30	0.74	—	7.15	0.7–0.8	7.04	0.72
<i>sym</i> -Benzenetriamine	7.00	0.66	—	—	—	—	—	—	—

magnitude as the observed values, but in comparison with the data by Farrell and Newton²⁶ they are slightly too large. For comparison the results of a recent semi-empirical calculation by Kwiatkowski²⁷ are also given.

Turner²⁰ has recently published IP data, including higher IP values of several molecules. Such data are compared to some calculated higher IP values in Table 8. Turner's values are obtained by photoelectron spectroscopy leading to adiabatic potentials. The lowest vertical potentials are usually very close to the adiabatic ones. In case of higher IP's, the values of the vertical potentials may be substantially higher than the adiabatic potentials, about 1 eV in several cases. In view of this the agreement between theory and observation, reported in Table 8, is rather satisfactory.

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

Molecule	IP (calc)	IP (obs) ²⁰
Pyridine	9.27	9.28
	9.72	—
	10.5	10.54
	12.78	12.22
Pyrrole	8.23	8.22
	9.08	9.03
	12.27	12.38
Aniline	7.66	7.71
	9.03	8.95
	10.17	10.49

We are going to extend the present computational scheme to more complex heteroatomic molecules, *e.g.* those found in the prosthetic groups of many enzymes.³ The knowledge of the ionization potential constitutes an important information, because it is correlated with the electron donor capacity of the molecule in charge transfer (EDA) complexes. As it may be difficult to obtain experimental IP values for these complex molecules it is gratifying to note that the absolute values of the calculated IP's in the present investigation are in very good agreement with experiments.

3. *Dipole moments.* The calculated values of the π -electron contribution to the dipole moment, μ_{π} , are given in Table 9. Of course no significance can

Table 9. Dipole moments. Calculated values of μ_{π} . Experimental values of μ_{total} . In Debye.

Molecules	Calc. μ_{π}	Obs. μ_{total}
Pyridine	0.33	2.25 ⁵⁶
Pyrimidine	0.38	2.44 ⁵⁶
Pyrrole	2.55	1.80 ³⁸
Aniline	1.60	1.53 ³⁹
<i>o</i> -Phenylenediamine	2.53	1.49 ⁵⁶
<i>m</i> -Phenylenediamine	1.58	1.72 ⁵⁶
<i>p</i> -Phenylenediamine	0	1.51 ⁵⁶
Indole	2.27	2.05 ⁴⁰
Carbazole	1.72	2.11 ⁵⁶
Phenanthrene	0.19	0 ⁵⁶
Quinoline	0.41	2.31 ⁵⁶
Isoquinoline	0.44	2.75 ⁵⁶
Azulene	2.33	1.08 ⁵⁶
10-Aza-azulene	3.29	—
Acridine	0.75	2.13 ⁵⁶

be given to these data as the contribution from sigma and lone pair electrons are missing. However, Smith²⁸ has estimated the mesomeric moment of aniline to be 1.67 Debye, in unexpectedly good agreement with our calculated value of 1.60 D. The experimental value of the total dipole moment of *p*-phenylenediamine is 1.51 D,⁵⁶ indicating a non-planar structure of the molecule. In the calculations this molecule was assumed planar like aniline.

4. *Electronic spectra.* The transition energies have been calculated by configurational interaction including all singly excited states. The oscillator strengths have been determined from the standard formula of Mulliken and Rieke.²⁹

In Tables 10–20 we present the results obtained together with available experimental data. The values collected in these tables under the heading "Observations" are in most cases estimated by us from the reported experimental data.

Table 10. Electronic transitions of amino-benzenes. For notations, see Table 3 and Fig. 1.

Calculation			Observations						
ν	f	pol	Kimura <i>et al.</i> ³⁰ vapour			Forbes and Leckie ⁴¹ in cyclohexane ^a		Godfrey and Murrell ⁴² in cyclohexane ^a	
			ν_{\max}	range	f	ν_{\max}	$\log \epsilon$	ν_{\max}	f
Aniline									
36.1	0.05	<i>x</i>	35.5	34-37	0.028	34.9 ^b	3.28	35.1 ^b	0.026
44.1	0.29	<i>y</i>	43.5	41-47	0.14	42.7-42.9 ^b	3.95	42.5 ^b	0.17
51.3	0.38	<i>x</i>	51.6	48-59	0.51			50.7	—
54.4	0.92	<i>y</i>	55.5	48-59	0.57				
60.0	0.69	<i>x</i>							
61.7	0.11	<i>y</i>	63.5 ^c	59-66	(0.68)				
<i>o</i> -Phenylenediamine									
34.6	0.08	<i>y</i>	—			34.6	3.54	34.0	0.039
40.7	0.17	<i>x</i>				42.5	3.82	41.9	0.11
49.2	0.42	<i>x</i>						45.9	—
49.9	0.95	<i>y</i>							
59.2	0.02	<i>x</i>							
59.3	0.31	<i>y</i>							
<i>m</i> -Phenylenediamine									
35.3	0.04	<i>x</i>	—			34.1	3.41	34.0	0.024
42.6	0.08	<i>y</i>				~41.7	3.84	41.9s	0.19
47.6	0.44	<i>y</i>						45.4	—
48.1	1.01	<i>x</i>							
57.6	0.11	<i>x</i>							
58.8	0.55	<i>y</i>							
<i>p</i> -Phenylenediamine									
33.0	0.11	<i>x</i>	—			31.7	3.30	32.7	0.038
41.6	0.44	<i>y</i>				40.7	3.93	41.0	0.17
49.6	0							49.5	—
53.0	0.45	<i>x</i>							
53.9	0								
54.4	1.01	<i>y</i>							
<i>sym</i> -Benzenetriamine									
35.1	0		—			—		35.5	—
42.0	0							42.7s	—
47.6	1.10	<i>xy</i>						45.3	—
50.7	0.0002	<i>xy</i>							
63.5	0.07	<i>xy</i>							
65.6	0								

^a No absorption curves published. ^b For solvent shifts in aniline; *cf.* Mangini.⁴³ ^c Two bands.

Table 11. Electronic transitions of *sym*-triazine. For notations, see Table 3.

Symmetry	Calculation		Observations			
	ν	f	Vapour ⁵⁷		Favini <i>et al.</i> ⁴⁹ in hexane	
			ν_{\max}	range	ν_{\max}	range
$^1A_2'$	45.7	0	~46	43-48	45.1	43-49
$^1A_1'$	57.1	0		57→	54.3s	52-57
$^1E'$	61.3	1.08				2.23

Table 12. Electronic transitions of quinoline. For notations, see Table 3 and Fig. 1.

Calculation			Observations									
ν	f	pol φ°	Mataga <i>et al.</i> ⁵⁸ in hexane			Favini <i>et al.</i> ⁴⁹ in hexane			Zimmermann <i>et al.</i> ⁵⁹ in ethanol			
			ν_{\max}	range	log ϵ	ν_{\max}	range	f	ν_{\max}	range	log ϵ	pol
	$n-\pi^*$											
34.5	0.008	z	33.2	(?)		—			—			
53.4	0.001	z				—			—			
	$\pi-\pi^*$											
33.9	0.05	-3	31.9	30-34	3.40	31.9	31-33	0.025	32.0	31-35	3.95	x
40.6	0.16	-81	37.3	35-40	3.65	37.0	34-39	0.12	36.0	34-39	3.6	y
47.4	0.14	-8				44.4	42-46	0.54	43.2	42-47	4.6	x
49.9	1.27	+11				49.1	46-55	0.93		47-49→	4.2	
50.8	0.72	-12										
52.2	0.65	-85										
53.4	0.15	+77										
68.2	0.29	+63										

Table 13. Electronic transitions of isoquinoline. For notations, see Table 3 and Fig. 1.

Calculation			Observations							
ν	f	pol. φ°	Favini <i>et al.</i> ⁴⁹ in hexane				Zimmermann <i>et al.</i> ⁵⁹ in ethanol			
			ν_{\max}	range	log ϵ	f	ν_{\max}	range	log ϵ	pol. ^a
	$n-\pi^*$									
35.7	0.008	z								
48.7	0.001	z								
	$\pi-\pi^*$									
34.4	0.02	+24	31.6	31-35	3.55	0.02	31.2	30-35	3.7	$y?$
40.1	0.24	+78					35.4	peak	3.4	$y?$
47.6	0.01	+48	37.6	36-39	3.62	0.11	37.0	35-42	3.5	$x?$
48.2	0.14	-6					43.2 s	42-43		y
50.3	1.84	-8	46.4	45-49	4.94	1.02	46.0	43-47	4.8	x
51.7	0.003	-17								
53.9	0.75	+74	~51 s	49-54	4.5					
67.8	0.30	+79								

^a Arguments are given for a reversal of the order of the L_a and L_b bands of isoquinoline in transition to methylamine and acrylonitrile, where experiments are still uncertain.

Table 14. Electronic transitions of azulene. For notations, see Table 3 and Fig. 1.

Calculation			Observations									
ν	f	pol	Kitagawa <i>et al.</i> ⁵³ Vapour			Mann <i>et al.</i> ⁵⁰ in heptane			Zimmermann <i>et al.</i> ⁵¹ in ethanol			
			ν_{\max}	range	f	ν_{\max}	range	f	ν_{\max}	range	log ϵ	pol
17.0	0.03	<i>y</i>	no obs. below			17.3	14–21	0.01	17.3	14–23	2.6	?
28.2	0.03	<i>x</i>	33 kK			29.3	25–30	0.08	29.4	28–33	3.9	<i>x</i>
36.0	0.17	<i>y</i>	33–36 w						33.9	peak	3.2	<i>y</i>
42.4	1.79	<i>x</i>	38.4	36–41	1.4	36.6	34–38	1.10	36.0	34–39	4.8	<i>x</i>
46.8	0.20	<i>y</i>	~42.5	41–46	m	42.3	40–44	0.38	42.1	40–45	4.3	<i>y</i>
50.8	0.18	<i>x</i>	48–58 Rydb.									
54.9	0.24	<i>y</i>										
56.6	0.46	<i>x</i>	~54	50–58		51.8 ^a	46–57	0.65				
57.5	0.81	<i>y</i>										
59.7	0.28	<i>y</i>										
65.3	0.13	<i>x</i>	~62	58–62	→							

^a Broad, flat absorption band.

Table 15. Electronic transitions of 10-aza-azulene. For notations, see Table 3 and Fig. 1.

Calculation			Observations ^a Los <i>et al.</i> ⁵² in solution	
ν	f	pol. φ°	ν_{\max}	log ϵ
19.8	0.03	+ 71	21.7	3.05
30.2	0.01	+ 56	30.3	3.40
			31.7	3.53
36.7	0.19	- 74		
44.0	1.91	0	38.0	4.60
48.1	0.44	- 88	44.6	4.15
51.6	0.13	- 2		
56.9	0.25	+ 20		
57.7	0.31	- 54		
59.7	0.32	+ 75		

^a No absorption curves published.

Table 16. Electronic transitions of indole. For notations, see Table 3 and Fig. 1.

Calculation			Observations					
ν	f	pol. φ°	Schütt and Zimmermann ⁴⁴ in ethanol			Klevens and Platt ¹⁶ in hexane		
			ν_{\max}	range	log ϵ	ν_{\max}	range	log ϵ
36.7	0.04	- 46	34.0 ^a	peak	3.9	34.5	peak	3.6
41.7	0.21	+ 46	35.5 ^a	35–43.5	3.8	~38	35–42.5	3.8
48.7	0.57	- 82	44.8	43.5–48.5→	4.6	46.7	43–48	4.4
49.6	0.34	- 32	45.9	43.5–48.5→				
53.1	0.85	+ 69				~52	48–57	5.6
55.0	0.22	+ 21						
56.6	0.24	- 21						

^a According to Schütt and Zimmermann⁴⁴ and Weber⁴⁵ the two lowest electronic transitions are differently polarized.

Table 17. Electronic transitions of carbazole. For notations, see Table 3 and Fig. 1.

Calculation			Observations						
ν	f	pol.	Schütt and Zimmermann ⁴⁴ in ethanol				Klevens and Platt ¹⁶ in solution		
			ν_{\max}	range	$\log \epsilon$	pol.	ν_{\max}	range	$\log \epsilon$
34.0	0.03	y	30.0	29.5–33	3.6	y	no obs. below 33 kK		
38.1	0.24	x	34.5	33–37	4.2	x	34.2	33–37	4.2
40.5	0.002	x	38.8	37–40	4.3	x	39.2	37.5–40	4.3
45.7	0.20	y				y ^a			
45.8	1.79	x	42.7	40–47	4.6		42.7	40–46	4.6
47.6	0.27	y							
50.8	0.02	x	~48	47–49.5	4.3		47.5	46–49	4.4
53.9	0.18	x					50	49–51	4.3
54.5	0.02	y							
56.9	0.98	y					52	→	
57.0	0.07	x							

^a The polarization spectrum is not measured beyond 42.5 kK.

Table 18. Electronic transitions of phenanthrene. For notations, see Table 3 and Fig. 1.

Calculation			Observations						
ν	f	pol.	Dehlor and Dörr ⁴⁶ in ethanol				Klevens and Platt ⁴⁷ in heptane		
			ν_{\max}	range	$\log \epsilon$	pol.	ν_{\max}	range	f
32.0	0.01	y	28.9	28.6–33	2.8	y	28–32	0.003	
37.9	0.36	x	34.0	33.5–34.5	4.5	x	33–36	0.18	
39.5	0.04	x	~36.5	35–37.5	4.3	x			
44.7	1.57	x	39.5	37.5–45	4.9	x	39.4	34–44	1.09
			41.3	37.5–45	4.8				
45.4	0.51	y							
46.5	0.03	y							
48.4	0.40	y	45.3	45–49→	4.5		45.2	44–51	
49.0	0.49	x	47.5	45–49→	4.6		47.1	44–51	0.6
52.6	0.02	y							
53.3	0.05	x							
55.6	0.09	x							
57.4	0.04	x							
57.9	0.24	y					53.4	51–56	0.59
59.1	0.25	y							
59.2	0.004	x							
60.9	0.53	y					57–59.5→	s?	

It should be noted that our parameter sets have been determined to fit vapour phase spectra of the small standard molecules, while most observed data in Tables 10–20 emanate from solution spectra. It is not possible to give an accurate quantitative estimate of the solvent effect. The solvent

Table 19. Electronic transitions of anthracene. For notations, see Table 3 and Fig. 1.

Calculation			Observations									
ν	f	pol	Refs. ^{63,64} Vapour			Klevens <i>et al.</i> ⁴⁷ in heptane			Zimmermann <i>et al.</i> ⁶¹ in ethanol			
			ν_{\max}	range	f	ν_{\max}	range	f	ν_{\max}	range	$\log \epsilon$	pol
32.6	0.28	<i>y</i>	27.5	26–33	0.013	26.4	25–33	0.10	26.6	26–34	4.1	<i>y</i>
30.2	0.08	<i>x</i>	28.9	26–33	0.024	28.6	25–33		27.6	26–34	4.1	
40.6	0								28.5		w	<i>x</i>
41.9	0								30.0		w	
43.7	0		40.8?	40–41		32.3?	32–35					
44.7	2.94	<i>x</i>	42.3	41–45	0.80– 1.15	39.6	36–44	2.28	39.5	38–44	5.2	<i>x</i>
46.3	0.03	<i>y</i>	no obs. between			45.3	44–50	0.28	46.1	44–48	3.9	<i>y</i>
49.7	0.005	<i>y</i>	45 and 53 kK									
50.5	0.002	<i>x</i>										
51.5	0.67	<i>y</i>	~55	53–57		53.7	51–58	0.65				
62.5	0.11	<i>x</i>										
64.1	1.17	<i>y</i>										

Table 20. Electronic transitions of acridine. For notations, see Table 3 and Fig. 1.

Calculation			Observations									
ν	f	pol.	Mataga <i>et al.</i> ⁵⁸ in benzene			Perkampus ⁶⁶ in methanol			Zanker <i>et al.</i> ⁶⁷ in ethanol, ethylether			
			ν_{\max}	range	$\log \epsilon$	pol.	ν_{\max}	range	$\log \epsilon$	ν_{\max}	range	$\log \epsilon$
33.3	0.23	<i>y</i>	26.5	25–33	3.54	<i>y</i>	26 s		3.45	25.3	25–26	3.5
29.8	0.30	<i>x</i>	28.8	25–33	3.88	<i>y</i>	28	26–32	3.9	28.1	25–34	4.2
38.8	0.01	<i>x</i>	27.9	26–33	4.02	<i>x</i>				35.3 s	35–37	2.8
42.3	0.001	<i>y</i>								39.7	39–42	5.3
45.9	2.39	<i>x</i>					40.2	38–45	5.2			
48.0	0.01	<i>x</i>										
48.0	0.01	<i>y</i>										
50.0	0.37	<i>y</i>					47	45–49	4.2	~47 ^a	44–50	4.1
51.7	0.31	<i>x</i>										
53.9	0.52	<i>y</i>										

^a Broad, flat absorption band.

shifts for the two lowest singlet transitions in aniline are $\sim 500 \text{ cm}^{-1}$ and 900 cm^{-1} , respectively, as reported in Table 10. In other cases the shifts are even larger, *cf.* Tables 14 and 19. With this effect in mind, we find a satisfactory overall agreement between calculated and observed spectral data.

In almost all cases where polarization data are available the results of our investigation agree with the experimental findings. The only exception is isoquinoline, where different assignments have been made by different authors; cf. Table 13.

No observation of the $n-\pi^*$ transitions of quinoline or isoquinoline have been published as far as we are aware. The explanation of the failure to find these bands seems to be that stronger $\pi-\pi^*$ bands cover the $n-\pi^*$ bands; cf. Tables 12 and 13.

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