

Semi-empirical Parameters in  $\pi$ -Electron Systems

## X. The Nitrogen-Nitrogen Bond and Nitrogen-Methyl Bond

O. GROPEN and P. N. SKANCKE

*Department of Chemistry, University of Oslo, Blindern, Oslo, Norway*

A modified Pariser-Parr-Pople approximation has been extended to include parameters appropriate to the nitrogen-nitrogen bond and the nitrogen-methyl bond. Predicted bond distances, ionization potentials, and electronic spectra which are based on the resultant parameter values, are in satisfactory agreement with available experimental results.

In the first paper of the present series a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation was introduced and applied to pure hydrocarbons.<sup>1</sup>

The method has later been extended to include different groups and hetero-atoms.<sup>2-9</sup>

The purpose of the present investigation is to extend the method further to include parameters appropriate to the nitrogen-nitrogen bond of the azine type, and to the bond between nitrogen and the methyl group. In the evaluation of the parameters appropriate to the latter bond, some auxiliary conditions not related directly to experimental information have been introduced. This has been done in order to avoid the use of the rather uncertain experimental information available.

## METHOD OF CALCULATION AND DETERMINATION OF PARAMETERS

The scheme applied for the evaluation of the semi-empirical parameters was introduced in the first paper of this series,<sup>1</sup> where also the symbols applied were defined.

Only the new parameters appropriate to the bonds treated in this investigation will be discussed here.

A characteristic assumption in this particular approach is the dependence of the one-electron parameter  $W_\mu$  on the surroundings to atom  $\mu$ . This dependence is expressed by

$$W_\mu = W_\mu^0 + \sum_\nu \Delta W_\mu(\nu) \quad (1)$$

where  $\Delta W_\mu(\nu)$  varies with the nature of the neighbouring atom  $\nu$  and also with the bond distance  $R_{\mu\nu}$  through the assumed linear relation

$$\Delta W_\mu(\nu) = \Delta W_\mu^0(\nu) + \delta_{\mu\nu}^W (R_{\mu\nu} - R_0) \quad (2)$$

In eqn. (2)  $\delta_{\mu\nu}^W$  is a parameter to be determined empirically, and  $R_0$  is a chosen reference distance for the bond between atoms  $\mu$  and  $\nu$ . The core resonance integral,  $\beta_{\mu\nu}$ , and the two-electron Coulomb integral,  $\gamma_{\mu\nu}$ , between nearest neighbours contribute two parameters each:

$$\beta_{\mu\nu} = \beta_{\mu\nu}^0 + \delta_{\mu\nu}^\beta (R_{\mu\nu} - R_0) \quad (3)$$

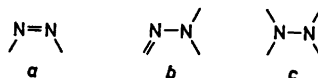
$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^0 + \delta_{\mu\nu}^\gamma (R_{\mu\nu} - R_0) \quad (4)$$

### Parameters for the nitrogen-nitrogen bond

In a previous paper of this series<sup>3</sup> treating the azines and the aromatic amines, a distinction was made between two types of nitrogen atoms, *viz.* those contributing one electron to the  $\pi$ -electron system (pyridine-nitrogen) and those yielding a lone pair of electrons (pyrrole-nitrogen). The same distinction is made here, and the same two reference values were chosen for the one-electron parameter  $W_N^0$ .

This distinction between the two kinds of nitrogen atoms leads to three different types of bonds between nitrogen atoms as shown in Fig. 1.

Fig. 1. The three different types of bonds between nitrogen atoms.



Although a separate evaluation of the two parameters  $\gamma$  and  $\beta$  for the three bonds in addition to the four possible  $\Delta W_N(N)$ -values would have been desirable, the lack of reliable experimental information has necessitated an estimate of some of them.

The parameters appropriate to bond type *a* were determined by use of experimental data for the molecule pyridazine. In order to evaluate the parameters for the other two types of nitrogen-nitrogen bonds certain assumptions had to be made.

The parameters necessary for bond type *a* are the two-center two-electron Coulomb repulsion integral, the core resonance integral, and the one-electron parameter  $\Delta W_N(N)$ .

In a vacuum UV-investigation of pyridazine the three lowest  $\pi \rightarrow \pi^*$  transitions were assigned to three absorption maxima at 241  $m\mu$ , 185  $m\mu$ , and 169  $m\mu$ , respectively.<sup>10</sup> The value of the transition energy corresponding to the absorption band at 185  $m\mu$  is rather uncertain, because of an  $n \rightarrow \pi^*$  transition which is expected to absorb in the same region. Therefore, only the transitions at 241  $m\mu$  and 169  $m\mu$  were used in the determination of the parameters. These two peak positions lead to transition energies of 5.13 eV and 7.33 eV, respectively.

A conclusive assignment of the measured ionization potentials of pyridazine seems to be very hard to obtain. In a presentation of adiabatic values in 1966 Turner<sup>11</sup> suggested the first  $\pi$ -electron potential to be at 10.55 eV. However, in a very recent study of the vertical potentials he has reached the conclusion that the only reliable  $\pi$ -electron potential is one at 13.59 eV.<sup>12</sup> These new results have furthermore lead to the conclusion that there are probably two  $\pi$ -electron potentials at lower energies, one in the region 9.30–9.80 eV and another in the region 10–11 eV.

Accordingly, we have in our present studies assumed the third  $\pi$ -electron potential to have the value 13.59 eV, and we have applied this value in the evaluation of the semi-empirical parameters. Thus three parameters are to be adjusted to three observables.

The remaining parameters necessary for the calculations are as far as possible taken from the previous papers of this series. The two-electron one-center Coulomb repulsion integrals  $\gamma_{\pi\pi}$  are taken from a previous work by one of us.<sup>13</sup> The two-electron integrals for non-nearest neighbours were determined by the uniformly charged sphere approximation,<sup>14</sup> with the orbital exponents of Coulson and Duncanson.<sup>15</sup> The parameters obtained are presented in Table 1. In Table 2 the calculated values for the three observables mentioned above are compared with the corresponding experimental values.

During the adjustment of the parameters for the nitrogen-nitrogen bond in pyridazine we found that a coupled variation of the parameters did not change the predicted values for the three observables significantly. This is illustrated by the data presented in Tables 3 and 4. The set of parameters

Table 1. Semi-empirical parameters for the N–N bond in pyridazine. All values in eV. For notations see text.

$R_{NN}^0 = 1.33 \text{ \AA}$					
$\gamma_{NN}$	=	15.44	$W_N^0$	=	-12.57
$\gamma_{N_1N_2}^0$	=	9.00	$\Delta W_{N_1}^0(N_2)$	=	-0.32
$\beta_{N_1N_2}^0$	=	-2.67			

Table 2. Comparison between calculated and experimental data applied in the evaluation of the semi-empirical parameters. All values in eV.

Molecule	IP <sub>(calc.)</sub>	IP <sub>(obs.)</sub>	$\Delta E$ <sub>(calc.)</sub>	$\Delta E$ <sub>(obs.)</sub>
Pyridazine	13.59	13.59 <sup>a</sup>	5.18 7.33	5.13 <sup>b</sup> 7.33

Observed values: <sup>a</sup> Ref.11. <sup>b</sup> Ref.10.

Table 3. Alternative parameters for the N—N bond in pyridazine. All values in eV. For comments see text.

$R_{\text{NN}}^0 = 1.33 \text{ \AA}$					
$\gamma_{\text{NN}}$	=	15.44	$W_{\text{N}}^0$	=	-12.57
$\gamma_{\text{N}_1\text{N}_2}^0$	=	7.50	$\Delta W_{\text{N}_1}^0(\text{N}_2)$	=	-0.82
$\beta_{\text{N}_1\text{N}_2}^0$	=	-2.85			

Table 4. Comparison between experimental data and data calculated by use of the parameters in Table 3. All values in eV.

Molecule	IP <sub>(calc.)</sub>	IP <sub>(obs.)</sub>	$\Delta E$ <sub>(calc.)</sub>	$\Delta E$ <sub>(obs.)</sub>
Pyridazine	13.64	13.59 <sup>a</sup>	5.20 7.30	5.13 <sup>b</sup> 7.33

Observed values: <sup>a</sup> Ref. 11. <sup>b</sup> Ref. 10.

given in Table 3 is obtained by the variation mentioned above, and the values predicted for the three observables are found in Table 4. A comparison between the results presented in Tables 2 and 4 indicates that the fitting to the available experimental values does not lead to a precise set of values for the parameters. This is particularly true for the two-electron integral.

Several assumptions have been made for the bond types *b* and *c*. In conformity with the Goepfert-Mayer-Sklar partitioning,<sup>16</sup> and the zero differential overlap approximation, the parameters  $\gamma_{\text{N}_i\text{N}_j}$  and  $\beta_{\text{N}_i\text{N}_j}$  have been assumed to be equal for the three bonds at a given distance. For the one-electron parameter  $\Delta W_{\text{N}}(\text{N})$  the situation is more complicated. In a previous study within this series we have determined the parameters for the nitroso- and nitro groups.<sup>7</sup> The values obtained for the one-electron parameter,  $W$ , appropriate to oxygen were -20.90 eV and -19.80 eV for the two groups, respectively. For the parameter  $\Delta W_{\text{N}}(\text{O})$  the values -0.32 eV and -1.82 eV were found for pyrrole- and pyridine nitrogen, respectively. The N—O bond distance is the same in these two groups.<sup>7</sup>

These results indicate that in a proper treatment of the parameters,  $\Delta W_{\text{N}}(\text{N})$  should have four distinct values depending on the different combinations of the two kinds of nitrogen atoms. Due to the rather limited experimental information available we had to make some simplifying assumptions. This led us to assume that a pyridine- and a pyrrole nitrogen exert the same influence on an adjacent nitrogen atom. On the other hand we have allowed the neighbouring effect on the pyridine nitrogen to be different from that on the pyrrole type.

In order to make the parameters in this work consistent with those obtained for the nitro- and the nitroso groups, the parameter  $\Delta W_{N_p}(N)$  where  $N_p$  is a pyrrole type nitrogen is evaluated from the following relation:

$$\frac{\Delta W_N(N)}{\Delta W_N(O)} = \frac{\Delta W_{N_p}(N)}{\Delta W_{N_p}(O)} \quad (5)$$

All the parameters for the diazine bond are based on a reference distance of 1.33 Å.

To make the parameters applicable for other internuclear distances, we have assumed the same distance dependence as for the carbon-carbon bond.<sup>1</sup> The procedure outlined above gives the set of parameters for the N-N bond presented in Table 5 where also the distance dependence parameters are included.

Table 5. All the semi-empirical parameters necessary for the nitrogen-nitrogen bond and the nitrogen-methyl bond.

Bond	Pyridine nitrogen		Pyrrole nitrogen	
Nitrogen-nitrogen	$R_{NN}^0$	= 1.33 Å	$R_{NN}^0$	1.33 Å
	$\gamma_{NN}$	= 15.44 eV	$\gamma_{NN}$	= 15.44 eV
	$\gamma_{N_1N_2}^0$	= 9.00 eV	$\gamma_{N_1N_2}^0$	= 9.00 eV
	$\delta_{N_1N_2}^\gamma$	= -3.99 eV/Å	$\delta_{N_1N_2}^\gamma$	= -3.99 eV/Å
	$\beta_{N_1N_2}^0$	= -2.67 eV	$\beta_{N_1N_2}^0$	= -2.67 eV
	$\delta_{N_1N_2}^\beta$	= 3.05 eV/Å	$\delta_{N_1N_2}^\beta$	= 3.05 eV/Å
	$W_N^0$	= -12.57 eV	$W_N^0$	= -8.52 eV
	$\Delta W_{N_1}^0(N_2)$	= -0.32 eV	$\Delta W_{N_1}^0(N_2)$	= -0.06 eV
	$\delta_{N_1N_2}^W$	= 9.22 eV/Å	$\delta_{N_1N_2}^W$	= 9.22 eV/Å
Nitrogen-methyl	$R_{N-CH_3}^0$	= 1.52 Å	$R_{N-CH_3}^0$	1.52 Å
	$\gamma_{CH_3,CH_3}$	= 10.01 eV	$\gamma_{CH_3,CH_3}$	= 10.01 eV
	$\gamma_{N,CH_3}^0$	= 5.65 eV	$\gamma_{N,CH_3}^0$	= 5.65 eV
	$\delta_{N,CH_3}^\gamma$	= -3.99 eV/Å	$\delta_{N,CH_3}^\gamma$	= -3.99 eV/Å
	$\beta_{N,CH_3}^0$	= -1.33 eV	$\beta_{N,CH_3}^0$	= -1.33 eV
	$\delta_{N,CH_3}^\beta$	= 3.05 eV/Å	$\delta_{N,CH_3}^\beta$	= 3.05 eV/Å
	$W_{CH_3}$	= -12.02 eV	$W_{CH_3}$	= -12.02 eV
	$\Delta W_N^0(CH_3)$	= 1.28 eV	$\Delta W_N^0(CH_3)$	= 0.23 eV
	$\delta_{N,CH_3}^W$	= 9.22 eV/Å	$\delta_{N,CH_3}^W$	= 9.22 eV/Å

A comparison of the obtained parameters with those evaluated for the previously studied atoms and groups within this particular modification of the PPP-approximation has not demonstrated any systematic dependency of these on orbital exponents, electronegativities or bond distances.

## Parameters for the methyl-nitrogen bond

In a study of hyperconjugation Roos<sup>2</sup> has developed a method within this scheme where he suggests that the phenomenon may be described by a quasi  $\pi$ -orbital located on the methyl group. This group was regarded as a heteroatom, and the appropriate parameters for this "heteroatom" bonded to a carbon atom were evaluated. The same procedure is here supposed to be suitable for the methyl group bonded to nitrogen. For this bond the parameters are not evaluated by a fitting to experimental data, but estimated by certain auxiliary assumptions. The one-center two-electron Coulomb integral,  $\gamma_{\text{CH}_3\text{CH}_3}$ , and the one-electron parameter,  $W_{\text{CH}_3}^0$ , are adopted from the work of Roos.<sup>2</sup> The reference values for the parameter  $W_{\text{N}}^0$  are those mentioned above, and quoted in Table 5.

The remaining parameters for the bond between the  $\text{CH}_3$  group and pyridine nitrogen are determined by assuming that the ratio between the parameter values for this bond and their counterparts for the N–O bond in the nitroso group is equal to the corresponding ratio between the parameter values for the C– $\text{CH}_3$  bond and the C–O bond in the carbonyl group.

For the parameters assigned to the bond between the  $\text{CH}_3$  group and pyrrole nitrogen, the same procedure was applied. Here the appropriate parameter values for the N–O bond in the nitro group were incorporated.

In these relations the necessary parameters were taken from other papers in this series.<sup>2,5,7</sup> The fact that both the C–O and the N–O bond distances are about 1.22 Å, and the  $\text{CH}_3$ –C distance is equal to around 1.52 Å makes it reasonable to assume that the  $\text{CH}_3$ –N parameters estimated by the relations above, should be valid for the same distance. To make them suitable for other distances, the distance parameters from the first paper<sup>1</sup> are used. All these parameters are presented in Table 5.

At this stage of the investigation we found it desirable to make a closer examination of the lack of precision in our parameter values. This was done in the following way.

Table 6. Calculated and observed transition energies for dimethylnitrosamine. Results for calculations with both the parameter sets mentioned in the text. All values in eV.

Molecule	$\Delta E_{(\text{obs.})}^a$	$\Delta E_{(\text{calc.})}$	
		Set 1	Set 2
Dimethyl-nitrosamine	5.47	5.77	4.88
	7.50	7.97	5.80

Observed values: <sup>a</sup> Ref. 17.

The procedures discussed above were used to calculate an additional set of parameters, based on the pyridazine values given in Table 3. This new set (called set 2) was used in a comparative prediction of the two lowest  $\pi \rightarrow \pi^*$

transitions in dimethylnitrosamine. The choice of this particular molecule was dictated by the requirement of exact and reliable experimental information.<sup>17</sup> The results, presented in Table 6, demonstrate clearly that the original set of parameters (called set 1), based on the pyridazine values in Table 1, and given in Table 5, are superior in reproducing these particular observables.

## RESULTS AND DISCUSSION

The parameter values obtained by the procedure outlined above, were used in a study of the electronic structure and the electronic spectra of a series of molecules. In addition to our test molecule pyridazine (I), the following molecules were included: *s*-tetrazine (II), nitroguanidine (III), nitrosamine (IV), nitroamine (V), nitrosomethane (VI), nitromethane (VII), dimethylnitrosamine (VIII), and dimethylnitroamine (IX). For labelling of molecules and notation of atoms, see Fig. 2.

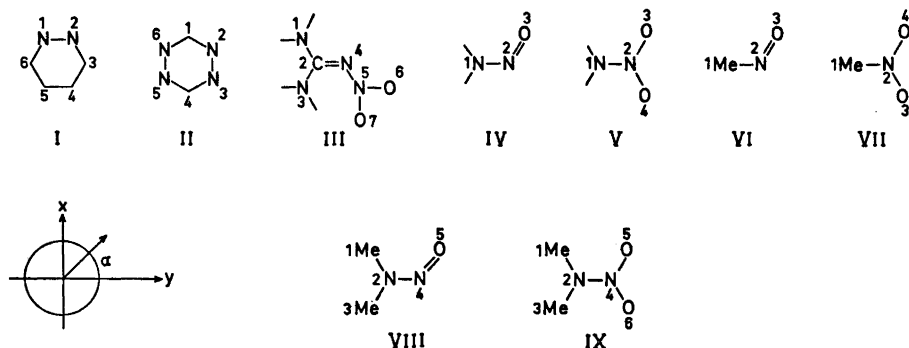


Fig. 2. Labelling of molecules and notation of atoms.

The results obtained are collected in Tables 7–11, where also available experimental data were included for comparison. The molecular geometries used are the experimentally determined ones where such are available. The remaining geometrical parameters were assumed. For nitroso- and nitroamine the geometrical parameters determined by the investigation of dimethylnitrosamine and dimethylnitroamine<sup>18,19</sup> were used.

## Ground state properties

The different kinds of bond distances were estimated from the calculated bond orders by means of the relations:

- 1)  $R_{\mu\nu}(\text{C,C}) = 1.517 - 0.18 p_{\mu\nu}$
- 2)  $R_{\mu\nu}(\text{C,N}) = 1.458 - 0.18 p_{\mu\nu}$
- 3)  $R_{\mu\nu}(\text{N,O}) = 1.325 - 0.18 p_{\mu\nu}$
- 4)  $R_{\mu\nu}(\text{N,N}) = 1.453 - 0.18 p_{\mu\nu}$

Table 7. Assumed, calculated and observed bond distances. All values in Å.

Molecule	Bond	$R_{\text{ass.}}$	$R_{\text{calc.}}$	$R_{\text{obs.}}$	
Pyridazine <sup>a</sup>	1-2	1.330	1.330	1.330	
	2-3	1.338	1.340		
	3-4	1.397	1.399		
	4-5	1.375	1.394		
<i>s</i> -Tetrazine <sup>b</sup>	1-2	1.338	1.341	1.338	
	2-3	1.330	1.328	1.330	
Nitro-guanidine <sup>c</sup>	1-2	1.340	1.367	1.340	
	2-3	1.340	1.363	1.340	
	2-4	1.350	1.347	1.350	
	4-5	1.350	1.360	1.350	
	5-6	1.230	1.218	1.230	
	5-7	1.220	1.227	1.220	
Nitrosamine	1-2	1.344	1.329		
	2-3	1.234	1.198		
Nitroamine <sup>d</sup>	1-2	1.382	1.350	1.427	
	2-3	1.223	1.223	1.206	
Nitrosomethane <sup>e</sup>	1-2	1.470	—	1.49	$p=0.3483$
	2-3	1.220	1.172	1.22	
Nitromethane <sup>f</sup>	1-2	1.470	—	1.46	$p=0.3064$
	2-3	1.220	1.206	1.21	
Dimethyl-nitrosamine <sup>g</sup>	1-2	1.461	—	1.461	$p=0.0937$
	2-3	1.461	—	1.461	$p=0.0834$
	2-4	1.344	1.323	1.344	
	4-5	1.235	1.206	1.235	
Dimethylnitro-amine <sup>h</sup>	1-2	1.461	—	1.461	$p=0.0472$
	2-4	1.382	1.352	1.382	
	4-5	1.223	1.223	1.223	

Observed values: <sup>a</sup> Ref. 20. <sup>b</sup> Ref. 32. <sup>c</sup> Ref. 33. <sup>d</sup> Ref. 22.  
<sup>e</sup> Ref. 21. <sup>f</sup> Ref. 34. <sup>g</sup> Ref. 19. <sup>h</sup> Ref. 18.

In these equations  $p_{\mu\nu}$  is the mobile bond order between the atoms  $\mu$  and  $\nu$ . Relations 1), 2), and 3) have been taken from previous studies in this series.<sup>1,3,7</sup> In the additional relation suggested here, we have arbitrarily assumed the value of 0.18 for the coefficient in front of the bond order. The constant term was obtained by relating the calculated bond order to the observed bond distance for the N—N bond in pyridazine.<sup>20</sup> As shown in Table 7, the predicted bond distances obtained by this procedure are in satisfactory agreement with available experimental data, except for a few cases.

The general trend in our results suggests that the N—O distances in the nitroso group is somewhat shorter than in the nitro group. The few available experimental data for the nitroso compounds are not in agreement with this result.<sup>19,21</sup>



To the authors' knowledge no experimentally determined structure is available for nitrosamine. For nitroamine, however, the geometry has been determined by a microwave investigation.<sup>22</sup> The N–N bond distance obtained by this study, 1.427 Å, is considerably longer than our predicted value of 1.35 Å. This discrepancy might, however, be interpreted in terms of the overall structure of the molecule as given by the microwave study. The four heavy atoms lie in one plane orthogonal to the plane through the two nitrogen atoms bisecting the angle HNH. The angle between the plane through the NH<sub>2</sub>-group and the N–NO<sub>2</sub> plane is, however, found to be 52°. Furthermore, the HNH angle has a value of 115°. These geometrical data clearly indicate that the assumed *sp*<sup>2</sup> hybridization on the nitrogen atom in the amino group is rather doubtful. The pyramidal arrangement around this atom may at least in part offer a reasonable interpretation of the discrepancy between the measured and the predicted N–N bond distance.

In the planar molecules dimethylnitrosamine and dimethylnitroamine the observed<sup>18,19</sup> bond distances are reproduced with a reasonable accuracy. The planarity of these molecules in contrast to nitroamine can hardly be explained in terms of hyperconjugation as the bond orders between the CH<sub>3</sub> groups and nitrogen are found to be very small; see Table 7. The observed difference between the N–N bond distances in these two molecules is nicely reproduced by our calculations. One might therefore conclude that this difference is explainable in terms of conjugation. By referring to the calculated bond orders one might conclude that the nitroso group is more electronegative than the nitro group. This difference in electronegativity has also been used in the interpretation of spectroscopic<sup>17</sup> and geometrical<sup>18</sup> studies.

From Table 7 it is seen that no correlation is found between calculated bond orders and measured lengths for the different bonds between nitrogen and methyl carbon. This fact clearly indicates that as far as these particular bonds are concerned, the model applied here is too simple.

The predicted molecular ionization potentials as estimated by Koopmans' theorem are given in Table 8. Unfortunately the experimental information available for comparison is both scarce and uncertain. In fact the only molecule for which measurements have been carried through is pyridazine.<sup>11,12</sup> As mentioned above the assignment of the experimental values for this molecule has shown to be extremely complicated. The most recent results indicate one  $\pi$ -electron potential in the region 9.30–9.80 eV and another one between 10 and 11 eV. The presence of these two  $\pi$ -electron potentials is strongly supported by our calculations as shown in Table 8. It should be emphasized that the two lowest  $\pi$ -electron potentials have not been used for the evaluation of the parameter values.

It is also very satisfactory that calculations performed within this same scheme for the non-bonding electrons,<sup>23</sup> predict the two lowest potentials for these electrons to be in the same interval (8–11 eV), because this also is in accordance with the tentative assignment of Turner.<sup>12</sup>

Other ground state properties considered here are the  $\pi$ -electron charges on the different atoms, and the  $\pi$ -electronic contribution to the dipole moments.

Table 8. Calculated and observed ionization potentials. All values in eV.

Molecule	IP <sub>(calc.)</sub>	IP <sub>(obs.)</sub> <sup>a</sup>
Pyridazine	9.62	9.30–9.80
	10.26	
	13.59	
<i>s</i> -Tetrazine	9.96	10–11
	11.42	
	14.33	
Nitro- guanidine	10.02	13.59
	10.66	
	11.16	
	13.61	
	15.60	
Nitroso- methane	12.27	
	15.24	
Nitros- amine	10.56	
	14.67	
Nitroamine	12.43	
	12.43	
	17.18	
Nitromethane	12.30	
	12.99	
	17.04	
Dimethyl- nitrosamine	10.30	
	12.65	
	13.43	
	16.10	
Dimethyl- nitroamine	11.31	
	12.39	
	13.44	
	14.69	
	17.53	

Observed values: <sup>a</sup> Ref. 11, 12.

The  $\pi$ -electron charges are presented in Table 9 together with "experimental" values for pyridazine.<sup>24</sup> Our calculated values for this molecule are in good agreement with the experimental values of Brown *et al.*<sup>24</sup> The  $\pi$ -electron charges for pyridazine obtained with the alternative parameter set given in Table 3 are also tabulated for comparison. The agreement between calculated and observed values is not so good for this case.

The charges on the dimethylamino group in dimethylnitrosamine are lower than on the same group in dimethylnitroamine. This indicates that the nitroso group within this approximation is a stronger electron-acceptor than the nitro group, which is in agreement with the bond order considerations made for the same molecules. The calculated dipole moments are collected in Table 10

Table 9. Calculated and "experimental"  $\pi$ -electron densities. For notation of atoms see Fig. 2.

Molecule/Atom	1	2	3	4	5	6	7
Pyridazine <sup>a</sup>	1.055	1.055	0.951	0.955			
Pyridazine <sup>b</sup>	1.088	1.088	0.925	0.987			
Pyridazine <sup>c</sup>	1.049	1.049	0.912	1.039			
s-Tetrazine	0.916	1.042					
Nitroguanidine	1.786	0.799	1.764	1.422	0.770	1.705	1.753
Nitrosamine	1.601	0.817	1.582				
Nitroamine	1.720	0.833	1.723				
Nitrosomethane	1.913	0.607	1.480				
Nitromethane	1.921	0.809	1.635				
Dimethylnitrosamine	1.982	1.524	1.985	0.907	1.602		
Dimethylnitroamine	1.992	1.731	1.992	0.830	1.728		

<sup>a</sup> Based on parameter set 1. <sup>b</sup> Based on parameter set 2. <sup>c</sup> Ref. 24.

Table 10. Calculated and observed dipole moments in debye units.

Molecule	( $\mu$ ) <sub>calc.</sub>	( $\mu$ ) <sub>obs.</sub>	Ref.
Pyridazine (set 1.)	0.670	3.97	35
Pyridazine (set 2.)	1.147		
Nitroguanidine	9.82	6.95	36
Nitrosamine	5.03	—	—
Nitroamine	5.39	3.78	37
Nitrosomethane	3.12	—	—
Nitromethane	3.85	3.44	38
Dimethylnitrosamine	5.78	4.01	39
Dimethylnitroamine	5.49	4.61	40

where also experimental values are included for comparison. A direct comparison of the two sets of values is in principle inconsistent as the contribution from the  $\sigma$ -electrons is neglected in our calculations.

### Electronic spectra

The electronic transition energies were calculated by configurational mixing of all singly excited configurations. The oscillator strengths have been estimated from the formula of Mulliken and Rieke.<sup>25</sup>

In Table 11 the calculated values are collected and compared with available experimental data.

Table 11. Calculated and observed electronic spectra. Transition energies in eV.

Molecule	Calc.			Obs.		
	pol. <sup>h</sup>	<i>E</i>	<i>f</i>	<i>E</i>	<i>f</i>	
Pyridazine <sup>a</sup>	<i>x</i>	5.18	0.01	5.13	0.02	
	<i>y</i>	6.55	0.14	6.67	0.10	
	<i>y</i>	7.33	1.02	7.33	1.00	
	<i>x</i>	7.62	1.06			
	<i>x</i>	9.02	0.00			
	<i>y</i>	9.36	0.02			
<i>s</i> -Tetrazine <sup>b</sup>	<i>y</i>	5.51	0.04	5.01	$\epsilon=3700$	
	<i>x</i>	6.78	0.32	6.47	$\epsilon=3000$	
	<i>x</i>	7.91	0.89			
	<i>y</i>	8.92	1.29			
Nitroguanidine <sup>c</sup>	155°	4.86	0.51	4.68	$\epsilon=17140$	
	120°	6.02	0.23	5.49	$\epsilon=9940$	
	42°	6.26	0.33			
	218°	8.24	0.17			
	129°	8.86	0.00			
Nitromethane <sup>d</sup>	<i>y</i>	5.97	0.16	6.24	$\log \epsilon=3.30$	
	<i>x</i>	6.59	0.50			
	<i>y</i>	9.62	0.03			
Nitroso- methane	212°	6.26	0.24			
	79°	8.84	0.27			
Nitroamine <sup>e</sup>	<i>y</i>	6.48	0.38	5.49		
	<i>x</i>	6.63	0.40			
	<i>y</i>	10.26	0.01			
Nitrosamine	213°	6.49	0.54			
	129°	9.38	0.20			
Dimethylnitro- amine <sup>f</sup>	<i>y</i>	5.88	0.35	5.15		
	<i>x</i>	6.64	0.39			
	<i>x</i>	8.63	0.03			
	<i>y</i>	9.16	0.02			
	<i>y</i>	10.98	0.02			
Dimethylnitros- amine <sup>g</sup>	204°	5.77	0.52	5.47	0.15	
	84°	7.97	0.16			7.50
	119°	8.51	0.04			
	327°	10.37	0.10			

Observed values: <sup>a</sup> Ref. 10. <sup>b</sup> Ref. 27. <sup>c</sup> Ref. 29. <sup>d</sup> Ref. 31. <sup>e</sup> Ref. 41. <sup>f</sup> Ref. 30. <sup>g</sup> Ref. 17. <sup>h</sup> The angles given in this column are defined as the angles between the transition moment vectors and the positive *y*-axis.

In a critical review Innes, Byrnes and Ross <sup>26</sup> have collected and discussed the available experimental data for some azabenzene. Their paper clearly shows that the electronic spectra of these molecules are very hard to interpret.

As mentioned above, a recent investigation of the vacuum UV-spectrum of pyridazine<sup>10</sup> has led to an assignment of the three lowest  $\pi \rightarrow \pi^*$  transitions to absorption maxima at 241 m $\mu$ , 185 m $\mu$ , and 169 m $\mu$ . This gives transition energies of 5.13 eV, 6.67 eV, and 7.33 eV, respectively. The peak at 185 m $\mu$  is supposed to contain both the  $\pi \rightarrow \pi^*$  transition and a  $n \rightarrow \pi^*$  transition. This fact makes an exact location of the position of the  $\pi \rightarrow \pi^*$  transition rather difficult. Thus the agreement between calculated and observed values has to be considered as satisfactory for this transition. In the experimental work no splitting of the band at 169 m $\mu$  is observed.<sup>10</sup> It seems, however, reasonable to suppose that the two calculated transitions at 7.33 eV and 7.62 eV are to be found in the same peak.

In an investigation of the vacuum UV-spectrum of *s*-tetrazine<sup>27</sup> a  $\pi \rightarrow \pi^*$  transition absorbing at 247 m $\mu$  is reported. This does not agree very well with our calculated value. It has been pointed out, however,<sup>28</sup> that an exact location of this transition is hard to obtain due to an  $n \rightarrow \pi^*$  transition which is expected to absorb in the same region. The transition at 191 m $\mu$  is uncertain.<sup>27</sup> But in spite of this supposed uncertainty, the agreement between observed and calculated value is in fact better for this transition than for the lowest one.

The UV-spectrum for nitroguanidine is measured in aqueous sulfuric acid,<sup>29</sup> and because of the high polarity of the nitro group in the molecule, it is difficult to make any comparison without knowing the solvent shift. The same argument applies to dimethylnitroamine, where the solvents are dioxan and water.<sup>30</sup>

Table 12. Molecular orbitals for nitromethane.

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$$\begin{aligned} \phi_1 &= 0.1979 \chi_{\text{CH}_3} + 0.6352 \chi_{\text{N}} + 0.5279(\chi_{\text{O}_1} + \chi_{\text{O}_2}) \\ \phi_2 &= \phantom{0.1979 \chi_{\text{CH}_3} + 0.6352 \chi_{\text{N}}} + 0.7071(\chi_{\text{O}_1} - \chi_{\text{O}_2}) \\ \phi_3 &= 0.9599 \chi_{\text{CH}_3} + 0.0286 \chi_{\text{N}} - 0.1972(\chi_{\text{O}_1} + \chi_{\text{O}_2}) \\ \phi_4 &= 0.1985 \chi_{\text{CH}_3} - 0.7718 \chi_{\text{N}} + 0.4272(\chi_{\text{O}_1} + \chi_{\text{O}_2}) \end{aligned}$$

The molecular orbitals obtained for nitromethane are given in Table 12. For symmetry reasons the only singly excited configurations that will mix in a configurational interaction calculation are  $\Psi(1 \rightarrow 4)$  and  $\Psi(3 \rightarrow 4)$ . The mixing coefficients are 0.98995, 0.14137 and  $-0.14137$ , 0.98995 for the two resulting states, respectively.

These numbers clearly demonstrate that for this molecule configurational mixing limited to singly excited configurations is of minor importance in the description of the excited molecular states.

The transition energies may therefore be regarded as pure transitions between molecular orbitals:

$$\begin{aligned} \phi_1 \rightarrow \phi_4 &: & 9.62 \text{ eV} \\ \phi_2 \rightarrow \phi_4 &: & 6.59 \text{ eV} \\ \phi_3 \rightarrow \phi_4 &: & 5.97 \text{ eV} \end{aligned}$$

In a vacuum UV-investigation of nitromethane one transition at 6.24 eV has been reported.<sup>31</sup> This transition is expected to be an internal  $\pi \rightarrow \pi^*$  transition within the nitro group. Our calculations, however, make it more reasonable to assume that the observed peak is containing both the internal transition at 6.59 eV and the charge-transfer transition at 5.97 eV.

In a vacuum UV-investigation of dimethylnitrosamine<sup>17</sup> a band at 227  $m\mu$  has been reported. This band is supposed to represent a 0-0 transition, and thus is expected to be at lower energy than our predicted vertical one. In the same paper it is reported a transition at 165  $m\mu$ . This band is mentioned as an absorption tail below 190  $m\mu$ , so the value is probably very uncertain.

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