ACTA CHEMICA SCANDINAVICA 23 (1969) 2685–2696

Semi-empirical Parameters in π-Electron Systems

VII. The Nitro- and Nitroso Groups

ODD GROPEN and P. N. SKANCKE

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

A modified Pariser-Parr-Pople approximation has been extended to include parameters appropriate to the nitro- and nitroso groups. 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 a series of previous papers [1–6] a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation has been introduced. In the first paper,[1] introducing the scheme, a treatment of pure, unsaturated hydrocarbons was given. The subsequent papers have dealt with extensions of the scheme embracing the methyl group,[2] azines and unsaturated amines,[3] chlorine derivatives,[4] the carbonyl group,[5] and ether oxygen.[6]

The purpose of the present investigation is to extend the method further to include parameters appropriate to the nitro group and the nitroso group.

DETERMINATION OF SEMI-EMPIRICAL PARAMETERS

The general scheme used in this particular modification of the Pariser-Parr-Pople approximation has been outlined in the first paper of this series,[1] where also the symbols applied were defined. Consequently, only the new features of the scheme related to the systems studied here will be presented.

A characteristic assumption in this particular approach is the dependence of the one-electron parameter W_μ on the surroundings to atom μ. This dependence was expressed by

$$W_\mu = W_\mu^\circ + \sum_\nu \Delta W_\mu(\nu) \qquad (1)$$

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

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

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 μ and ν.

In a previous paper of this series treating the azines and aromatic amines, Fischer-Hjalmars and Sundbom [3] distinguished between two types of nitrogen atoms *viz.* those contributing one electron to the π-electron system (pyridine nitrogen) and those yielding a lone pair (pyrrole nitrogen). This distinction, which also is made here, does lead to two different reference values $W_\mu{}^\circ$ for nitrogen.

The experimental material available on bond distances supports the assumption that in the molecules studied here the differences between the N—O bond distances are small enough to be neglected. Due to this assumption the second term in eqn. (2) vanishes, and we are left with the constant terms $\Delta W_\mu{}^\circ(\nu)$.

For nitrogen we have adopted the $W_N{}^\circ$ values obtained by Fischer-Hjalmars and Sundbom.[3] Accordingly we have to determine the following parameters pertinent to the nitrogen atom: $\Delta W_N{}^\circ(O)_{nitro}$ and $\Delta W_N{}^\circ(O)_{nitroso}$

Because of the assumption of a fixed N—O bond distance, we obtain two constant W-values for the oxygen atom, one for the nitro-group oxygen, and one for the nitroso-group oxygen.

The same assumptions concerning the bond distances have been made also by the empirical determination of the core-resonance integrals and the two-electron two-center Coulomb repulsion integrals. In conformity with the Goeppert-Mayer-Sklar partitioning [7] and the zero differential overlap approximation, the parameters γ_{NO} and β_{NO} have been assumed to be equal for the nitro- and the nitroso group.

The one-center two-electron Coulomb integral values have been taken from a previous work by one of us.[8] The two-electron integrals for non-nearest neighbours were determined by the uniformly charged sphere approximation with the orbital exponents of Coulson and Duncanson.[9]

Additional parameters necessary for the calculations performed here have been taken from the previous papers in the series.[1-6]

Thus there are altogether six parameters to be determined from experimental data: $\Delta W_N{}^\circ(O)_{nitro}$, $\Delta W_N{}^\circ(O)_{nitroso}$, $W_O(nitro)$, $W_O(nitroso)$, β_{NO}, and γ_{NO}.

The numerical values of the parameters were determined by a least squares fit to experimental data for the molecules nitrobenzene (I) and nitrosobenzene (II).

In a vacuum UV investigation of nitrobenzene the two lowest $\pi \rightarrow \pi^*$ transitions have been assigned to a very weak observed band at 280 mμ and to a band of medium intensity at 240 mμ, respectively.[10] The peak positions recorded have led to observed transition energies at 4.38 eV and 5.11 eV, respectively. As the low-energy band showing vibrational structure is perturbed by the dominating peak of the 240 mμ band, its exact position is somewhat uncertain. The direction of the dipole moment of the corresponding transition is, however, known.[10]

We have used these two transition energies for the determination of the parameter values.

In the case of nitrosobenzene a rather recent study of the absorption spectrum in heptane solution and in vapour has been reported.[11] Unfortunately, only one band position in the vapour spectrum is given numerically in the paper. This is the weak band corresponding to the lowest $\pi \rightarrow \pi^*$ transition energy. The remaining part of the vapour spectrum is presented by a graph from which exact peak positions are hard to locate. By comparing the presented vapour and solution spectra we have therefore made the assumption that the vapour values are 0.1 eV higher than the corresponding solution values. These corrected solution values were found to be in rather good agreement with estimates based on the graph of the vapour spectrum.

We used the three lowest $\pi \rightarrow \pi^*$ transition energies for the determination of the semi-empirical parameter values. The values used for the two highest of the applied transitions are mean values based on two different vibrational transitions.[11]

The choice made of test molecules and of electronic transitions for the numerical evaluation of semi-empirical parameters is governed by the requirements to reliability and exactness of the available experimental information. To avoid systematic errors due to solvent shifts we prefer to use vapour spectra. For all the experimental transitions applied here the assignments are rather conclusive.[10,11]

The experimental ionization potentials applied for the determination of semi-empirical parameters, are the recently measured values of Turner *et al.*[12] These values, 10.26 eV and 9.97 eV for nitro- and nitrosobenzene, respectively, correspond to vertical ionization processes. The use of these values introduces a slight inconsistency in the parameter scheme as the potentials used for the determination of parameters in the previous papers of this series have been adiabatic ones. We do, however, find it advantageous to use experimental values for which the assignments are conclusive. Furthermore, the differences between adiabatic and vertical values are rather small for a series of monosubstituted benzenes.[12,13]

Table 1. Semi-empirical parameters for the nitro group. All values in eV. For notation, see text.

$\gamma_{OO} = 18.89$	$\beta_{NO} = -2.37$
	$W_N^\circ = -8.52$
$\gamma_{NN} = 15.43$	$\Delta W_N^\circ(O) = -0.32$
$\gamma_{NO} = 9.25$	$W_O = -19.80$

Table 2. Semi-empirical parameters for the nitroso group. All values in eV. For notation, see text.

$\gamma_{OO} = 18.89$	$\beta_{NO} = -2.37$
	$W_N^\circ = -12.57$
$\gamma_{NN} = 15.43$	$\Delta W_N^\circ(O) = -1.82$
$\gamma_{NO} = 9.25$	$W_O = -20.90$

Table 3. Comparison between calculated and experimental data applied in the evaluation of the semi-empirical parameters. All values in eV.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$	$\Delta E_{calc.}$	$\Delta E_{obs.}$
I	10.24	10.26[a]	4.55	4.38[b]
			5.08	5.11[b]
II	9.97	9.97[a]	4.06	4.20[c]
			4.70	4.61[c]
			5.90	5.73[c]

[a] Ref. 12; [b] Ref. 10; [c] Ref. 11.

Thus we have altogether seven observables to which six parameters are to be adjusted. The parameter-values obtained by the fitting are presented in Tables 1 and 2. In Table 3 the calculated values for the seven observables mentioned above are compared with the corresponding experimental values.

As revealed in Table 3 the agreement between predicted and observed quantities is very good. The largest discrepancy (0.17 eV) we find for the lowest $\pi \rightarrow \pi^*$ transition in nitrobenzene and for the third band in nitrosobenzene. As mentioned above the former is observed only as a shoulder on the peak of the much stronger transition at 5.11 eV, and the latter represents a corrected solution value. The measured oscillator strengths for these two transitions in nitrobenzene are 0.01 and 0.17, respectively. We avoided the use of the higher very strong bands observed for this molecule as they most certainly are composite bands containing several transitions.

Also in nitrosobenzene the lowest observed $\pi \rightarrow \pi^*$ transition suffers from the same uncertainties as mentioned for the nitro compound.

The numerical solutions of the SCF-equations were evaluated on a CDC 3300 computer by means of a programme written by Drs. B. Roos and T. Alm and kindly put at our disposal. The solutions for the molecular ground states were based on a single determinant, whereas configurational mixing embracing all the singly excited configurations was performed for the electronically excited states.

RESULTS AND DISCUSSION

The parameter-values obtained by the procedure mentioned above, were used in a study of the electronic structure and electronic spectra of a series of molecules. In addition to our two test molecules we have studied *p*-nitrotoluene (III), *p*-nitroaniline (IV), *m*-nitrotoluene (V), *p*-nitrosotoluene (VI), and *p*-nitrosoaniline (VII).

The results obtained are collected in Tables 4—8 where also available experimental data are included for comparison. The molecular geometries used by the evaluation of the parameter values, are the experimentally determined ones where such are available. The remaining geometrical parameters have been assumed.

For the derivatives of nitrobenzene, we have assumed the same bond distances in the nitro group and in the benzene ring as the observed values for nitrobenzene itself.[14] For the remaining molecules a benzene structure of the rings has been assumed.

No experimental values seem to be available for nitrosobenzene and its derivatives studied here. We have assumed the N—O bond distance in the nitroso group to be 1.22 Å, a value which is rather close to the corresponding distance in the nitro group.

For the C—C distance between the ring and the CH_3 group, we have used the value applied by Roos in his study of hyperconjugation.[15]

1. *Ground state properties.* The different kinds of bond distances were estimated from the calculated bond orders by means of the relations

$$R_{\mu\nu}(\mathrm{C,C}) = 1.517 - 0.18\ p_{\mu\nu} \quad (3)$$

$$R_{\mu\nu}(\mathrm{C,N}) = 1.458 - 0.18\ p_{\mu\nu} \quad (4)$$

$$R_{\mu\nu}(\mathrm{N,O}) = 1.325 - 0.18\ p_{\mu\nu} \quad (5)$$

In eqns. (3)—(5) $p_{\mu\nu}$ is the mobile bond order between atoms μ and ν. Relations (3) and (4) have been taken from previous studies in this series.[1,3] 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 determined by relating our calculated bond order to the observed bond distance for the N—O bond in nitrobenzene.

As shown in Table 4, the predicted bond distances obtained by this procedure are in satisfactory agreement with available experimental data, except for a few cases. Our predicted bond distances in nitrobenzene do not reproduce the observed geometry [14] of the hexagonal ring. The pronounced deviations from a benzene-like structure of the ring reported by Trotter [14] cannot be accounted for by our calculations. Our calculated C—N bond distance in nitrobenzene is also significantly shorter than the measured value. A more recent X-ray crystallographic investigation of *p*-nitroaniline has demonstrated the existence of a very long C—N bond distance also in this molecule.[16] This particular bond distance is also not reproduced by our calculations. On the other hand, formula (4) applied for the estimate of C—N bond distances, has previously been used by Fischer-Hjalmars and Sundbom who obtained a very good agreement with experiments for a series of molecules.[3] Therefore the discrepancies found in our cases are most likely related to perturbations of the σ-skeleton not accounted for in our calculations. The significant deviations of valence angles from 120° observed [14,16] in the hexagonal rings support this assumption. A further evidence for a pronounced conjugation across the C—N bond in nitrobenzene in its ground state is provided by interpretation of its electronic spectrum.[10]

Our predicted N—O bond distances are equal within a range of 0.03 Å. This result supports our assumption of a constant N—O distance in the evaluation of the parameter values. The general trend in our results suggests that the N—O distance in the nitroso group is somewhat shorter than in the nitro group. Unfortunately, there are not sufficient accurate experimental data available for the nitroso compounds to confirm this prediction.

Table 4. Assumed, calculated and observed bond distances. All values in Å.

Molecule	Bond	$R_{ass.}$	$R_{calc.}$	$R_{obs.}$
I[a]	1—2	1.208	1.208	1.208
	2—4	1.486	1.416	1.486
	4—5	1.367	1.401	1.367
	5—6	1.426	1.399	1.426
	6—7	1.363	1.396	1.363
II	1—2	1.22	1.182	
	2—3	1.40	1.380	
	3—4	1.40	1.409	
	4—5	1.40	1.396	
	5—6	1.40	1.397	
	6—7	1.40	1.400	
	7—8	1.40	1.393	
	3—8	1.40	1.411	
III	1—2	1.208	1.209	
	2—4	1.486	1.415	
	4—5	1.367	1.401	
	5—6	1.426	1.399	
	6—7	1.363	1.398	
	7—8	1.52		
IV[b]	1—2	1.208	1.210	1.246
	2—4	1.486	1.412	1.460
	4—5	1.367	1.402	1.400
	5—6	1.426	1.397	1.377
	6—7	1.363	1.408	1.401
	7—8	1.370	1.382	1.371
V	1—2	1.208	1.209	
	2—3	1.208	1.209	
	2—4	1.486	1.415	
	4—5	1.367	1.401	
	5—6	1.426	1.400	
	6—7	1.52	—	
	6—8	1.363	1.399	
	8—9	1.363	1.394	
	9—10	1.426	1.400	
	4—10	1.367	1.400	
VI	1—2	1.22	1.186	
	2—3	1.40	1.372	
	3—4	1.40	1.414	
	4—5	1.40	1.399	
	5—6	1.40	1.398	
	6—7	1.52		
	6—8	1.40	1.405	
	8—9	1.40	1.390	
	3—9	1.40	1.414	
VII	1—2	1.22	1.184	
	2—3	1.40	1.377	
	3—4	1.40	1.411	
	4—5	1.40	1.394	
	5—6	1.40	1.403	
	6—7	1.37	1.403	
	6—8	1.40	1.406	
	3—9	1.40	1.412	
	8—9	1.40	1.391	

Observed R-values: [a] Ref. 14; [b] Ref. 16.

Table 5. Calculated and observed ionization potentials. All values in e*V*.

Molecule	$(IP)_{calc.}$	$(IP)_{obs.}$
I	(10.24)	10.26[a] 10.18[b]
	10.32	
	13.08	
II	(9.97)	9.97[a]
	10.02	
	12.90	
III	9.87	9.82[b]
	10.19	
	12.47	
IV	8.28	8.85[b]
	9.96	
	11.31	
V	9.69	
	10.03	
	12.44	
VI	9.46	
	9.80	
	12.16	
VII	9.30	
	9.89	
	12.13	

Observed values: [a] Ref. 12; [b] Ref. 17.
Values in parentheses used by the adjustment of parameters.

The values of the molecular ionization potentials estimated by using Koopmans' theorem are presented in Table 5. The lowest potentials for nitrobenzene and nitrosobenzene, used by the adjustment of the parameters, are included for the sake of completeness. As shown in the table, the two lowest potential values for each of the test molecules are lying very close. The calculated spacings are 0.08 eV and 0.05 eV for the nitro and nitroso compound, respectively. This result is in accordance with the recent measurements of Turner where no splitting of the band of lowest ionization energy was observed.[12] This does imply that the assumed experimental potential values used in our adjustment of the parameters in reality are mean values of the two lowest potentials in each case. Due to the very small splitting this error should not be of any significance.

The experimental values quoted for *p*-nitrotoluene (III) and *p*-nitroaniline (IV) have been obtained by mass spectrometric measurements.[17] The splitting of the degenerate π-electron levels in benzene caused by the substituent CH_3 is observed to be around 0.2 eV, whereas the corresponding value for NH_2 as substituent is around 1.1 eV.[12] If this difference between the observed

splittings is assumed to be valid for (III) and (IV), an assumption supported by the calculated values shown in Table 5, the large discrepancy between calculated and observed values for (IV) may be due to the fact that the experimental value reported is an average of the two lowest potentials.

Other ground state properties considered here are the π-electronic charges on the different atoms and the π-electron contribution to the electric dipole moments. As revealed by Table 6, the calculated charges are rather high for the oxygen and nitrogen atoms in all the molecules studied. The predicted negative charge on the oxygen atoms, 0.5—0.7 electrons, is about the same as found in a study of carbonyl compounds performed in a previous paper of this series.[5]

Table 6. Calculated atomic π-electron charges.

	Atom									
Molecule	1	2	3	4	5	6	7	8	9	10
I	1.668	0.718	1.668	0.833	1.091	0.936	1.059	0.936	1.091	
II	1.494	0.699	0.981	0.911	0.996	0.945	0.998	0.967		
III	1.670	0.719	1.670	0.844	1.087	0.975	0.995	1.979	0.975	1.087
IV	1.675	0.724	1.675	0.868	1.073	1.040	1.020	1.814	1.040	1.073
V	1.671	0.717	1.670	0.844	1.126	0.924	1.976	0.983	0.984	1.104
VI	1.518	0.718	1.039	0.753	1.100	0.884	1.974	1.055	0.959	
VII	1.504	0.708	0.994	0.902	1.042	0.940	1.910	1.041	0.958	

Table 7. Calculated and observed dipole moments. In Debye units.

Molecule	$(\mu_\pi)_{calc.}$	$(\mu)_{obs.}$	Ref.
I	3.93	4.28	18
II	4.36	3.17	19
III	4.52	4.47	20
IV	6.34	5.60; 7.16	21; 22
V	4.83	4.17	23
VI	5.56	3.82	24
VII	4.89	—	

The calculated dipole moments are collected in Table 7, 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 σ-electrons is neglected in our calculation.

2. *Electronic spectra.* The electronic transition energies were calculated by configurational mixing including all singly excited configurations. The oscillator strengths have been estimated from the formula of Mulliken and Rieke.[25]

Table 8. Calculated and observed electronic spectra. Transition energies in eV.

Molecule	Calculated values			Observed values	
	ΔE	f	pol.[e]	ΔE	f
I[a]	(4.55)[g]	0.003	y	4.38	0.01
	(5.08)	0.26	x	5.11	0.17
	5.73	0.12	y		
	6.34	0.45	x	6.42	0.38
	6.52	0.15	y		
	7.38	0.53	x	7.56	0.87
	7.42	1.37	y		
	8.20	0.001	x		
	8.54	0.01	y		
	8.72	0.40	x		
II[b,h]	(4.06)	0.06	33°	4.20	0.08
	(4.70)	0.60	103°	4.61	0.20
	(5.90)	0.18	181°	5.73	0.09
	6.52	0.54	285°	6.46	0.26
	7.20	0.28	97°	7.20	0.83
	7.30	0.66	9°		
	7.53	0.12	97°		
	8.69	0.01	180°		
III[c]	4.53	0.001	y		
	4.91	0.29	x	5.09	log $\varepsilon = 4.00$
	5.64	0.17	y		
	6.32	0.39	x		
	6.53	0.20	y		
	7.20	0.61	x		
	7.45	1.22	y		
IV	4.07	0.06	y	3.84[c]; 3.88[d]	log $\varepsilon = 4.17$[c]
	4.20	0.42	x	4.60	
	5.30	0.16	y	5.45; 5.52	log $\varepsilon = 3.89$
	5.66	0.02	x		
	6.50	0.84	x		
	6.50	0.21	y		
	6.77	0.00	y		
	6.83	0.10	x		
	7.69	1.10	y		
V[c]	4.46	0.02	96°	4.15	log $\varepsilon = 3.08$
	4.93	0.24	276°	4.83	log $\varepsilon = 3.92$
	5.57	0.19	22°		
	6.23	0.45	266°		
	6.52	0.15	1°		
	7.30	0.71	45°		
	7.45	1.11	17°		
VI[b]	4.04	0.15	275°	3.99	$\varepsilon \approx 8800$
	4.69	0.59	290°	4.34	$\varepsilon \approx 9900$
	5.83	0.15	181°	5.40	$\varepsilon \approx 5900$
				5.52	$\varepsilon \approx 6800$
	6.50	0.42	112°		
	7.03	0.46	87°		

Table 8. Continued.

	7.21	0.59	12°		
	7.47	0.15	313°		
VII[b]	4.11	0.05	233°	3.35	$\varepsilon \approx 16\,700$
	4.47	0.68	292°	4.75	$\varepsilon \approx 4\,200$
	5.66	0.27	181°		
	6.36	0.22	302°		
	6.88	0.73	90°		
	7.24	0.12	62°		
	7.29	0.51	350°		

Observed values: *a* Ref. 10; *b* Ref. 11; *c* Ref. 26; *d* Ref. 27.

[e] The angles given in this column are defined as the angles between the transition moment vectors and the positive *y*-axis. See Fig. 1.

[g] Values in parentheses indicate transitions used for the adjustment of parameters.

[h] The observed *f*-values refer to measurements in heptane solution.

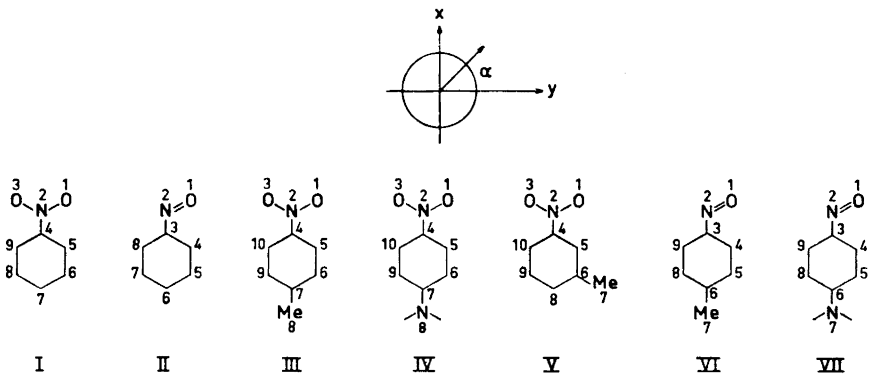

Fig. 1. Labelling of molecules and notation of atoms.

In Table 8 our calculated values are collected and compared with available experimental data. The calculated values in parentheses in the table indicate the transitions used by the fitting of the parameters. They are included here for the sake of completeness.

In the case of nitrobenzene the lowest transition shows the largest discrepancy. As mentioned above this absorption band is very weak, and it appears only as a shoulder on the dominating neighbour peak. Thus the experimental uncertainty here is rather large.

By comparing the predicted transitions with the measured spectrum of this molecule we find that the medium intensity band observed at 193 mμ does contain three different transitions. This absorption peak is also observed to have a shoulder. According to our results the high intensity band at 164 mμ is due to two rather close-lying transitions. This interpretation of the electronic spectrum of nitrobenzene is in accordance with previous calculations.[10]

The discussion of the electronic spectrum of nitrosobenzene is complicated by the fact that all the vapour-phase transition energies except the lowest one are estimated by us from solution data, and from a diagram given in the experimental paper.[11]

The exact position of the peak maximum of the weak band at around 300 mμ is hard to locate as this band has a very low intensity in the vapour-phase spectrum. The experimental oscillator strengths for the transitions in this molecule, quoted in Table 8, refer to measurements in heptane.[11] The *f*-value for the lowest transition is strongly diminished in the vapour-phase measurements.

We have adopted a value of 4.20 eV for the lowest $\pi \rightarrow \pi^*$ singlet-singlet transition. This value corresponds to the experimental peak maximum at 294 mμ. The remaining transition energies quoted in the table have been obtained by raising the observed energy values in heptane by 0.1 eV.

In view of the uncertainties inherent in the experimental data used by the adjustment of parameters, the agreement between experimental and predicted values for this molecule has to be considered as very good.

For the remaining molecules studied here, the experimental information is rather scarce. The experimental spectra quoted in the table refer to measurements in solution. Due to the presence of highly polar groups in the molecules, it is to be expected that the observed bands are rather sensitive to solvent effects. Bearing this in mind the general trend in the predicted values has to be considered as very satisfactory.

REFERENCES

1. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
2. Roos, B. *Acta Chem. Scand.* **21** (1967) 2318.
3. Fischer-Hjalmars, I. and Sundbom, M. *Acta Chem. Scand.* **22** (1968) 607.
4. Grabe, B. *Acta Chem. Scand.* **22** (1968) 2237.
5. Jensen, H. and Skancke, P. N. *Acta Chem. Scand.* **22** (1968) 2899.
6. Höjer, G. *Acta Chem. Scand.* **23** (1969) 2589.
7. Goeppert-Mayer, M. and Sklar, A. L. *J. Chem. Phys.* **6** (1938) 645.
8. Skancke, P. N. *Arkiv Fysik* **29** (1965) 573.
9. Duncanson, W. E. and Coulson, C. A. *Proc. Roy. Soc. (Edinburgh)* **A 62** (1943/49) 37.
10. Nagakura, S., Kojima, M. and Maruyama, Y. *J. Mol. Spectry.* **13** (1964) 174.
11. Tabei, K. and Nagakura, S. *Bull Chem. Soc. Japan* **38** (1965) 965.
12. Baker, A. D., May, D. P. and Turner, D. W. *J. Chem. Soc.* **B 1968** 22.
13. Turner, D. W. *Advan. Phys. Org. Chem.* **4** (1966) 31.
14. Trotter, J. *Acta Cryst.* **12** (1959) 884.
15. Roos, B. *Acta Chem. Scand.* **21** (1967) 2318.
16. Trueblood, K. N., Goldish, E. and Donohue, J. *Acta Cryst.* **14** (1961) 1009.
17. Crable, G. F. and Kearns, G. L. *J. Phys. Chem.* **66** (1962) 436.
18. Le Fevre, R. J. W. and Russel, P. *J. Chem. Soc.* **1936** 491.
19. Hammick, D. L., New R. G. A. and Sutton, L. E. *J. Chem. Soc.* **1932** 742.
20. Tiganik, L. *Z. physik. Chem.* **B 13** (1931) 425.
21. Wohlwill, M. *Z. physik. Chem.* **80** (1933) 67.
22. Phadke, S. R., Gokhale, S. D., Phalnikar, N. L. and Bhide, B. V. *J. Indian Chem. Soc.* **22** (1945) 239.

23. Poltz, H. *Z. physik. Chem.* **B 17** (1932) 155.
24. Tsuzuki, Y. and Higaski, K. *Sci. Papers Inst. Phys.-Chem. Research (Tokyo)* **39** (1941) 185.
25. Mulliken, R. S. and Rieke, C. A. *Rept. Progr. Phys.* **8** (1941) 231.
26. Kiss, A. I. and Horvath, G. *Acta Chim. Hung.* **42** (1964) 15.
27. Tanaka, J. *Bull. Chem. Soc. Japan* **36** (1963) 833.

Received February 21, 1969.