Theoret. chim. Acta (Berl.) 13, 171—174 (1969)

A CNDO CI Study of the Electronic Structure and Spectrum of Nitrobenzene

B. TINLAND

Section de Recherches de Mécanique Ondulatoire Appliquée, Faculté des Sciences de Lyon
69 Villeurbanne, France

Received January 23, 1969

The electronic spectrum of nitrobenzene is investigated by means of the modified CNDO method of Del Bene and Jaffé.

A number of semi-empirical methods for approximation to full LCAO-SCF calculations have been developed in recent years. Of these, the CNDO method of Pople and coworkers limited to valence-shell electrons is of particular interest since it takes proper account of electronic repulsion and introduces the simplifying ZDO approximation into the Roothaan equations [20, 21, 22, 23, 25, 26].

Several attempts to apply the original CNDO parametrization to the calculation of electronic spectra have failed recently and have shown the intermingling of σ and π states [4, 5, 10]. A modification of the CNDO/2 method was therefore finally suggested by Del Bene and Jaffé [6] who introduced the following modifications in the parametrization:

a) the one-center Coulomb integrals γ_{AA} were approximated as in the Pariser-Parr-Pople method [17, 18, 24] by the difference between the ionization potential and the electron affinity of valence orbitals. The two-center integrals γ_{AB} were computed by means of Pariser's interpolation formula [17];

b) the resonance integrals were evaluated as

$$\beta_{\mu\nu} = \tfrac{1}{2}k(\beta_A^\circ + \beta_B^\circ)S_{\mu\nu}$$

where β_A° and k are purely empirical parameters, with $k = 1$ for σ-type overlap and $k = 0.585$ for π-type overlap. The parameters were calibrated to reproduce the spectra of benzene and a few related molecules. They are summarized in Table 1.

It must be noticed that the introduction of the additional parameter k violates the invariance conditions. This new parametrization is therefore only applicable to planar molecules.

Other Pariser-Parr-Pople-like parametrizations of the CNDO equations have been attempted, such as those of Sichel and Whitehead [28, 29] and of Clark [2, 3] but these theories were not suitable for the calculation of spectra.

Table 1. *Parameter values (eV)*

	H	C	N	O
β_A°	−12.	−17.	−26.	−45.
γ_{AA}	12.85	11.11	12.01	13.0

The electronic structure and spectrum of nitrobenzene have been the subject of a number of experimental and theoretical studies [1, 7, 8, 9, 11, 13, 14, 15, 16, 19, 27, 30, 32, 33, 34, 35, 37]. We applied the modified CNDO method of Del Bene and Jaffé to this molecule and refined the computed spectrum by means of a configuration interaction calculation limited to the 30 lowest singly excited transitions. The geometry used is indicated in Table 2.

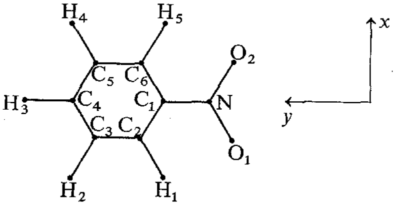

Fig. 1. Numbering scheme and coordinates axes

The observed and computed singlet transition energies are summarized in Table 3 together with some other results from various authors for comparison. It

Table 2. *Atomic coordinates* (Å)

Atom	*x*	*y*
O_1	−0.62320	0.
N	0.	1.03718
C_1	0.	2.52718
C_2	−1.22068	3.14914
C_3	−1.19573	4.57893
C_4	0.	5.24862
H_1	−2.14643	0.66444
H_2	−2.12629	5.12707
H_3	0.	6.32862

Table 3. *Singlet transition energies (eV), oscillator strengths and polarizations*

Experimental data [11, 36]	this work		[1]	[13]	[16]
y 3.86 (0.03)	*y* 3.60 (0.05)	$\pi\rightarrow\pi^*$, $\sigma\rightarrow\sigma^*$	3.94 (0.23)		
~3.91 (sh.)	3.93 (0.)	$\sigma\rightarrow\pi^*$	3.92 (0.02)		
~4.15 (sh.)					
x ~4.32 (sh.)	*x* 4.60 (0.39)	$\sigma\rightarrow\pi^*$			
y 4.93 (0.23)	*y* 4.93 (0.45)	$\pi\rightarrow\pi^*$, $\sigma\rightarrow\sigma^*$	5.34 (0.16)	4.95 (0.28)	4.57 (0.02)
			5.34 (0.34)	5.17 (0.20)	5.14 (0.48)
	x 5.34 (0.04)	$\pi\rightarrow\pi^*$			
5.83 (0.07)	*x* 5.77 (0.22)	$\sigma\rightarrow\pi^*$	5.66 (0.26)		5.87 (0.08)
5.95 (0.08)	*y* 5.93 (0.36)	$\sigma\rightarrow\pi^*$			
				6.47 (0.08)	
				6.49 (0.30)	
6.30 (0.42)	*x* 6.02 (1.09)	$\pi\rightarrow\pi^*$, $\sigma\rightarrow\sigma^*$	6.66 (0.27)	6.63 (0.70)	6.63 (0.60)
					6.77 (0.31)

may be seen that our values are in satisfactory agreement with the experimental ones and that the polarization directions are correct. The assignment of the bands is not obvious because the configuration interaction has the effect that the resulting transitions have not in general pure $\pi \rightarrow \pi^*$ or $\sigma \rightarrow \sigma^*$ or $\sigma \rightarrow \pi^*$ character. It is however clear that the main bands located at 4.93 eV and 6.30 eV gave a marked $\pi \rightarrow \pi^*$ character, which is satisfactory.

The experimental molecular ionization potential is 10.15 eV while the computed value is 8.25 eV by applying Koopman's theorem.

We obtained for the dipole moment the value 3.25 debyes which agrees with the experimental one: 2.51 d. $\leqq \mu_{\text{exp}} \leqq$ 4.32 d. [12].

The electron populations are finally given in Table 4.

Table 4. *Valence electrons populations*

	O_1	N	C_1	C_2	C_3	C_4	H_1	H_2	H_3
1*s*							1.11	0.99	0.99
2*s*	1.62	1.22	1.08	1.41	1.03	1.06			
$2p_x$	1.09	1.10	1.18	1.26	0.95	1.07			
$2p_y$	1.26	0.99	0.72	1.08	1.00	1.01			
$2p_z$	1.94	1.38	0.68	0.56	1.14	0.64			
Total	5.91	4.68	3.66	4.31	4.12	3.78	1.11	0.99	0.99

References

1. Bonnet, M.: Theoret. chim. Acta (Berl.) **11**, 361 (1968).
2. Clark, D. T.: Theoret. chim. Acta (Berl.) **10**, 111 (1968).
3. — Tetrahedron **24**, 2663, 3285 (1968).
4. Clark, P. A., and J. L. Ragle: J. chem. Physics **46**, 4235 (1967).
5. — J. chem. Physics **48**, 4795 (1968).
6. Del Bene, J., and H. H. Jaffé: J. chem. Physics **48**, 1807, 4050 (1968).
7. Doub, L., and J. M. Vandenbelt: J. Amer. chem. Soc. **69**, 2714 (1947).
8. Fernandez, J.: Comptes Rendus Acad. Sci. 233, 403 (1951).
9. Godfrey, M., and J. N. Murrell: Proc. chem. Soc. (London) **1961**, 171.
10. Kuznesof, P. M., and D. F. Shriver: J. Amer. chem. Soc. **90**, 1683 (1968).
11. Labhart, H., and G. Wagniere: Helv. chim. Acta **46**, 1314 (1963).
12. McClellan, A. L.: Tables of experimental dipole moments. San Francisco: W. H. Freeman 1963.
13. Matsuoka, O., and Y I'Haya: Molecular Physics **8**, 455 (1964).
14. Nagakura, S., and J. Tanaka: J. chem. Physics **22**, 236 (1954).
15. — J. chem. Physics **23**, 1441 (1955).
16. — M. Kojima, and Y. Maruyama: J. molecular Spectroscopy **13**, 174 (1964).
17. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
18. — J. chem. Physics **24**, 250 (1956).
19. Peacock, T. E.: Proc. physic. Soc. **78**, 460 (1961).
20. Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43**, S 129 (1965).
21. —, and G. A. Segal: J. chem. Physics **43**, S 136 (1965).
22. — — J. chem. Physics **44**, 3289 (1966).
23. — D. L. Beveridge, and N. S. Ostlund: Int. J. quant. Chem. **1S**, 293 (1967).
24. — Trans. Faraday Soc. **49**, 1375 (1953).
25. Roothaan, C. C. J.: Rev. mod. Physics **23**, 161 (1951).
26. Santry, D. P., and G. A. Segal: J. chem. Physics **47**, 158 (1967).
27. Schubert, W. M., and J. Robins: J. Amer. chem. Soc. **80**, 559 (1958).

28. Sichel, J. M., and M. A. Whitehead: Theoret. chim. Acta (Berl.) **7**, 32 (1967).
29. —— Theoret. chim. Acta (Berl.) **11**, 220, 239, 254, 263 (1968).
30. Simonetta, M., and A. Vaciago: Nuovo Cimento **11**, 596 (1954).
31. Tables of interatomic distances and configuration in molecules and ions. London: The Chemical Society 1958.
32. Tanaka, J.: Nippon Kagasu Zasshi **79**, 1114 (1958).
33. Trotter, J.: Canad. J. Chem. **37**, 351, 905 (1959).
34. — Tetrahedron **8**, 13 (1959).
35. Ungnade, H. E.: J. Amer. chem. Soc. **75**, 432 (1953).
36. UV spectra of organic compounds. Weinheim: Verlag Chemie 1966.
37. Wheland, G. W., and L. Pauling: J. Amer. chem. Soc. **57**, 2085 (1935).

Dr. B. Tinland
Centre de Mécanique Ondulatoire Appliquée
23, rue du Maroc, Paris XIX, France