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Authors

Hendrickson, David N.
Kuznesof, Paul M.

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David N. Hendrickson and Paul M. Kuznesof

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CNDO Calculations: Electronic Spectra and Nitrogen-14 N.M.R. Shielding Constants for Some Small Nitrogen Ions.

David N. Hendrickson and Paul M. Kuznesof

Department of Chemistry of the University of California and
the Inorganic Materials Research Division
of the Lawrence Radiation Laboratory,
Berkeley, California 94720

Abstract

The ^{14}N chemical shifts of the series NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^-, and NH_4^+ have been calculated using CNDO molecular orbitals. The required average energies ΔE were obtained by a simple virtual orbital method. The electronic spectra of the nitrite, nitrate and cyanide ions are discussed.

Introduction

The independent electron molecular orbital theory of diamagnetism applied to ^{13}C and ^{19}F NMR chemical shifts has given satisfactory agreement with experimental data.[1,4,7,13] The same method has been reported to reproduce the ^{14}N chemical shifts in linear[8,19] and sp^2-hybridized[7] nitrogen-containing molecules and ions, employing π - only LCAO molecular orbitals. Also, the large nitrogen and proton chemical shifts between pyridine and the pyridinium ion have been explained assuming a distribution of the σ - electrons.[6] However, Emsley[4] has shown recently that within the CNDO molecular orbital framework[14] (i.e. no assumption concerning the σ - electron distribution) the calculated nitrogen chemical shift between pyridine and the pyridinium ion is practically zero.

Application of Pople's theory of chemical shifts requires a knowledge of the electronic charge distribution in the ground state of the molecule as well as an average excitation energy, ΔE, for the magnetically allowed transitions. A common factor of all the above mentioned applications of Pople's theory is an assumption concerning the required ΔE value. The present CNDO calculations were undertaken to obtain the electronic excitation energies by a simple virtual orbital method for a series of small nitrogen ions: NO_2^-, NO_3^-, NO_2^+, CN^-, N_3^-, and NH_4^+. This approximate description of the excited states coupled with the ground state atomic charges from CNDO molecular orbitals provides a basis for testing the ability of the chemical shift theory to reproduce the observed ^{14}N chemical shift range (approximately 600 ppm)[3] for the above series of ions.

Calculations

Modified CNDO/1 calculations were performed on a CDC 6400 computer using a Fortran IV program.[10] Details and approximations for the calculations of molecular orbital eigenvectors, eigenvalues, electronic state wave functions, and excitation energies are given in Reference 10. In all cases except the nitrate ion the configuration interaction included all possible one electron determinants resultant from the filled and virtual molecular orbitals. The three lowest filled molecular orbitals of the nitrate ion were not used in the configuration interaction calculation for the nitrate ion.

Calculations of the ^{14}N shielding constants were performed considering only the "paramagnetic" contribution. Neglecting the two-center integrals and using the average energy approximation, the mean value of the local paramagnetic chemical shielding tensor for atom A has the form[7]

$$\sigma_p^{AA} = -\frac{e^2h^2}{2m^2c^2(\Delta E)_{av.}}\left\langle r^{-3}\right\rangle_{2p}\sum_B Q_{AB} \qquad (1)$$

where

$$Q_{AB} = \frac{4}{3}\delta_{AB}\left(P_{x_Ax_B} + P_{y_Ay_B} + P_{z_Az_B}\right) \qquad (2)$$

$$-\frac{2}{3}\left(P_{y_Ay_B}P_{z_Az_B} + P_{z_Az_B}P_{x_Ax_B} + P_{x_Ax_B}P_{y_Ay_B}\right)$$

$$-\frac{2}{3}\left(P_{y_Az_B}P_{z_Ay_B} + P_{z_Ax_B}P_{x_Az_B} + P_{x_Ay_B}P_{y_Ax_B}\right)$$

Here, the $P_{\mu\nu}$ are charge-density bond-order matrix elements for the 2p orbitals on atoms A or B. The average excitation energies $(\Delta E)_{av.}$ for the magnetically allowed transitions were taken as the eigenvalue of the lowest electronic state of proper symmetry. Any possible localization of the excitation on particular atoms was ignored. The average inverse cubic radius for a nitrogen 2p electron was calculated as

$$\langle r^{-3} \rangle_{2p} = \frac{1}{3} (Z_A/2a_o)^3 \qquad (3)$$

where Z_A is the nuclear charge obtained by Slater's rules considering the net electron density ρ_A on the nitrogen atom A

$$Z_A = 3.90 - 0.35 (\rho_A - 1)$$

Results and Discussion

Electronic Spectra

Nitrite ion - Experimentally determined bond lengths and angles, r_{NO} = 1.23Å and $\measuredangle$ ONO = 116°,[18] were used in the calculation of the electronic spectrum. The calculated and experimental transition energies and oscillator strengths for the nitrite ion are listed in Table I. Only the lowest calculated transition energies of each symmetry are included in the table.

In an earlier calculation, McEwen[11] assigned the observed nitrite transition energies at 3.50, 4.20, and 5.95 ev to symmetries of $^1B_1$,

TABLE I.

Electronic Transitions for the Nitrite, Nitrate, and Cyanide Ions

Ion	Symmetry	Energy(ev) and Oscillator Strength[a]
NO_2^-	$^1B_1$	2.16(3.50); 7.22; 8.31 .0024(.0005)[b]
	$^1A_2$	3.59(4.20); 5.92; 13.1 0(0.0004)[b]
	$^1B_2$	4.91(5.95); 10.2; 14.4 0.038(0.20)[b]
	$^1A_1$	6.03; 7.96; 11.1 0.0046
NO_3^-	$^1E'$	4.39(4.10); 6.34(6.26); 10.8 0.0054(.0001); 0.25(0.15)[b]
	$^1A_2'$	4.56; 10.6; 16.2
	$^1A_1'$	12.2
	$^1E''$	4.06; 4.84; 9.89
	$^1A_1''$	5.45

Table I (continued)

Ion	Symmetry	Energy(ev) and Oscillator Strength[a]
CN^-	$^1\Pi$	5.69(3.92); 11.5; 12.4 0.013(---)[c]
	$^1\Delta$	7.46
	$^1\Sigma^-$	7.46
	$^1\Sigma^+$	9.27; 16.2; 19.1

a. Only the lowest calculated transition energies are given; experimental values follow in parentheses. In some cases the oscillator strengths, both calculated and observed, are listed immediately below the corresponding transition energy.

b. See Reference 11.

c. This work.

$^1A_2$, and $^1B_2$, respectively. The spacing of the three corresponding transitions in Table I is the same as that obtained by McEwen within 4%. In addition, two more states of low energy are predicted, one allowed at 6.03 ev($^1A_1$) and one forbidden at 5.92 ev($^1A_2$). Considering the calculated and observed oscillator strengths for the various transitions, the assignment proposed by McEwen seems most reasonable. Thus, assignment of the calculated 4.91 ev($^1B_2$) transition to the observed band at 4.20 ev is precluded due to the large calculated oscillator strength. The experimental work of Strickler and Kasha[16] has also shown that the same assignment is reasonable on the basis of solvent effects on the absorption spectrum of nitrite. Possibly the calculated 6.03 ev($^1A_1$) band is the high energy shoulder on the 5.95 ev band observed by Strickler and Kasha in the nitrite spectrum in acetonitrile.

Nitrate ion - Calculations were carried out assuming D_{3h} symmetry and with $r_{NO} = 1.21\text{Å}$.[18] Two allowed transitions, both of E' symmetry, are predicted as shown in Table I. The lower energy E' transition arises from a low energy a_1^* antibonding orbital originally suggested by McEwen[11] to account for the lower energy band in the electronic spectrum. The calculated oscillator strengths for both E' transitions exceed the corresponding experimental values, but qualitative agreement is all that is expected.[12] Both nitrate bands have been observed[15] to have E' polarization in agreement with the above assignments. Strickler and Kasha[17] have made an alternate assignment for the lower energy band on the basis of the effects of solvent and temperature. They assign the

4.10 ev band as the highly forbidden n→ π* transition of A_1'' symmetry. According to our calculations this assignment is unsatisfactory.

Cyanide ion - The carbon-nitrogen bond distance was taken as 1.13Å, the value obtained in the crystal structure of KCN.[18] CNDO molecular orbitals and energies were calculated and the ordering of the molecular orbitals is compared in Figure I with that obtained by an ab initio calculation.[22] In the latter case a "double zeta plus polarization basis" was used,[2] where the polarization consisted of one 3dσ and one 3dπ function for the carbon and nitrogen with orbital exponents of 1.70, 1.80, 1.90 and 2.00, respectively. No optimization of orbital exponents was attempted, for it is reasonable to expect the molecular orbital energies would be close to convergence. As seen in Figure I, the CNDO ordering is quite similar to the ab initio ordering for the cyanide ion.

For the cyanide ion the ultraviolet region shows one peak at 3.92 ev shouldering on the end absorption.[23] Calculated transition energies and the calculated oscillator strength for the allowed $^1\Pi$ transition at 5.69 ev are listed in Table II. It seems reasonable to assign the observed band at 3.92 ev to the lowest calculated $^1\Pi$ transition energy. It was not possible to determine an oscillator strength for this band, but the molar extinction coefficient was found to be approximately 2.0 ℓ/mole-cm.

Azide, Ammonium, and Nitryl ions - Molecular dimensions obtained in standard structure determinations[18] were used for the calculations on the azide, ammonium, and nitryl ions. The calculated transition

TABLE II.

Electronic Transitions for the Cyanide, Ammonium, Azide, and Nitryl Ions.

Ion	Symmetry	Energy(ev)
NH_4^+	$^1T_2$	9.40; 23.1; 30.5
	$^1T_1$	22.5
	$^1E_1$	22.5
	$^1A_1$	25.4; 34.4
N_3^-	$^1\Pi_g$	3.69; 7.08; 17.5
	$^1\Sigma_g^-$	9.77
	$^1\Sigma_g^+$	12.0; 17.1; 22.4
	$^1\Delta_g$	9.78
	$^1\Pi_u$	8.61; 12.3; 13.3
	$^1\Sigma_u^-$	2.62
	$^1\Sigma_u^+$	6.94; 15.8; 19.8
	$^1\Delta_u$	26.2

Table II. (continued)

Ion	Symmetry	Energy(ev)
NO_2^+	$^1\Pi_g$	3.78; 7.23; 16.6
	$^1\Sigma_g^+$	8.60
	$^1\Sigma_g^+$	11.3; 17.2; 24.2
	$^1\Delta_g$	8.60
	$^1\Pi_u$	7.92; 13.4; 14.4
	$^1\Sigma_u^-$	4.37
	$^1\Sigma_u^+$	6.81; 17.5; 22.4
	$^1\Delta_u$	4.37

energies for these ions are listed in Table II. No experimental data are available as a check on the calculations.

^{14}N-Shielding Constants

The usual applications of Equation (1) for the calculation of chemical shifts for a series of structurally similar molecules involves the assumption of one ΔE value for all molecules. Often, a "reasonable" adjustment in ΔE is made. However, for the diversified series of ions under study here, the ΔE's were chosen as the eigenvalue for the lowest electronic state of proper symmetry; only very qualitative agreement between calculated and observed ^{14}N-chemical shifts were obtained (Column 6, Table III).

The disparities in the qualitative trend between our calculated and the observed chemical shifts may be attributed, at least in part, to differences in the effectiveness of the amount of configuration interaction considered for each ion. Thus, for the electronic spectrum of cyanide ion, the calculation for the lowest electric dipole transition gives an energy 1.77 ev in excess of the value determined for the only peak observed. On the other hand, for the nitrite ion the experimental transition energies exceed their corresponding calculated values; as a result the calculated nitrogen chemical shift between nitrite and cyanide ions is too large. Accordingly, adjustment of the ΔE value for the nitrite ion to 3.0 ev will improve the quantitative agreement in many cases. A better ΔE could be obtained if a weighted average of the eigenvalues for the lowest electronic states of proper symmetry was used.

TABLE III

Calculated and Observed ^{14}N Chemical Shifts

Ion	$\sum_B Q_{AB}$	$\langle r^{-3} \rangle_{2p}$	(ΔE) (ev)	$-\sigma_p$(calc.) ($\times 10^6$)	δcalc. (ppm)	δobs.[a] (ppm)
NO_2^-	2.878	2.539	2.16	2453	≡0	≡0
NO_3^-	2.934	2.768	4.06	1450	1003	254
NO_2^+	2.564	3.039	3.78	1494	958	260
CN^-	2.186	2.143	5.69	597	1856	380
N_3^- inner	2.493	2.537	3.69	1243	1210	383
N_3^- outer	2.247	2.124	3.69	938	1515	532
NH_4^+	1.901	2.498	22.5	153	2300	600

a. See References 3 and 20.

This would require more refined excited state eigenfunctions and transition energies, secured possibly by using an improved virtual orbital approach.[9]

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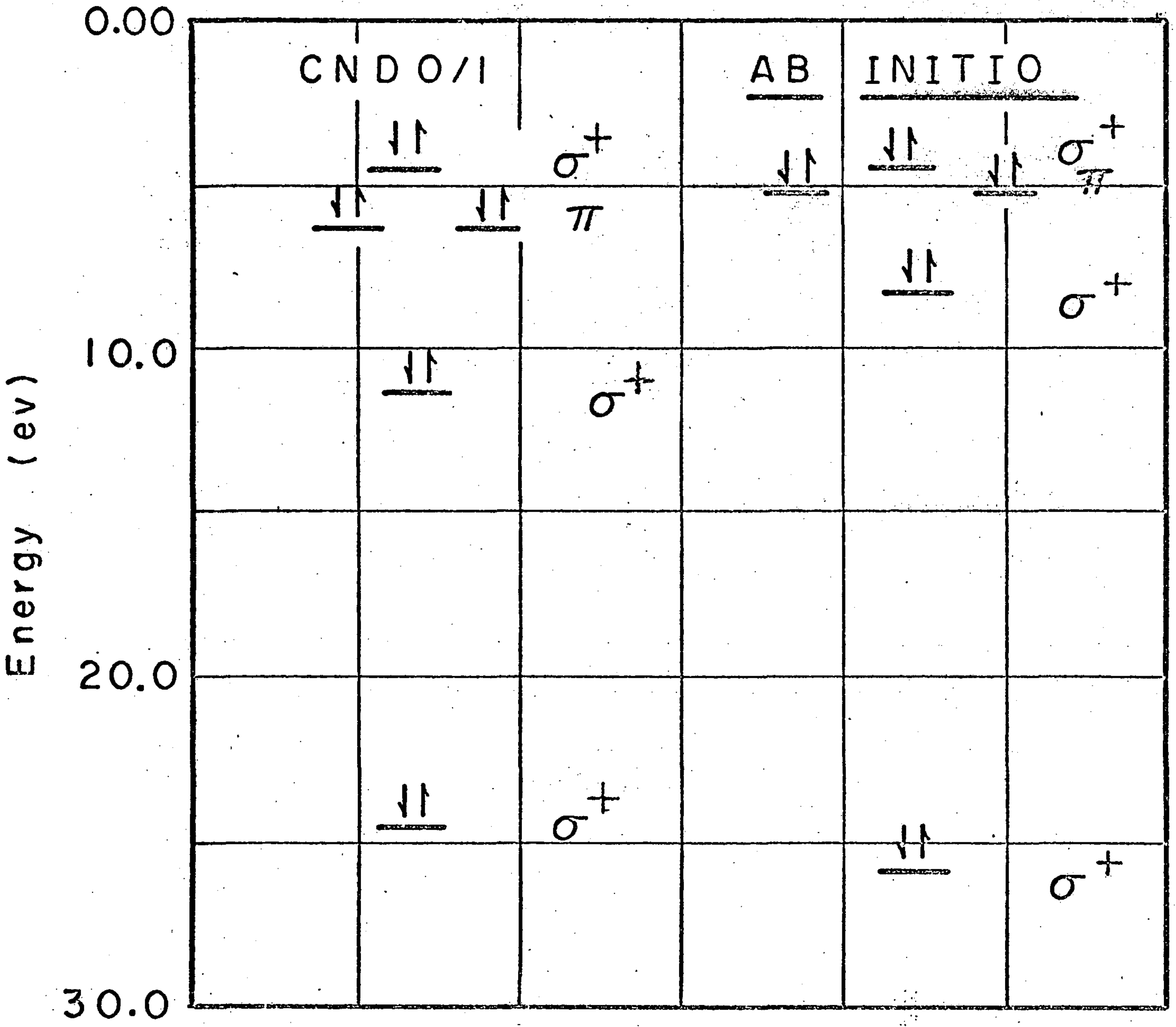

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Figure 1. Comparison of the Filled Molecular Orbital Energies Obtained by CNDO/1 vs. those by an *ab initio* method for the cyanide ion.

References

1. Bloor, J. E., and D. L. Breen, J. Phys. Chem., 72, 716 (1968).
2. Clementi, E., Tables of Atomic Functions, (International Business Machines Corporation, 1965).
3. Emsley, J. W., J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, (Pergamon Press, London, 2, 1966), pp. 1031-41.
4. Emsley, J. W., J. Chem. Soc. (A), 1387 (1968).
5. Emsley, J. W., J. Chem. Soc. (A), 2018, 2735 (1968).
6. Gil,V. M. S., and J. N. Murrell, Trans. Faraday Soc., 60, 248 (1964).
7. Karplus, M., and J. A. Pople, J. Chem. Phys., 38, 2803 (1963).
8. Kent, J. E., and L. Wagner, J. Chem. Phys., 44, 3530 (1966).
9. Kroto, H., and D. Santry, J. Chem Phys., 47, 792 (1967).
10. Kuznesof, P. M., and D. F. Shriver, J. Am. Chem. Soc., 90, 1683 (1968). Ph. D. thesis of P. M. Kuznesof, Northwestern University, 1967.
11. McEwen, K. L., J. Chem. Phys., 32, 1801 (1961).
12. Mulliken, R. S., and C. A. Rieke, Rept. Progr. Phys., 8, 231 (1941).
13. Pople, J. A., Mol. Phys., 7, 301 (1964).
14. Pople, J. A., D. P. Santry, and G. A. Segal, J. Chem. Phys., 43, S129, S136 (1965).
15. Sayre, E., J. Chem. Phys., 31, 73 (1959).
16. Strickler, S. J., and M. Kasha, J. Am. Chem. Soc., 85, 2899 (1963).
17. Strickler, S. J., and M. Kasha, Molecular Orbitals in Chemistry, Physics, and Biology, (Per-Olov Löwden, ed., Academic Press, New York, 1964).

18. Sutton, L. E., editor, Special Publication No. 11, The Chemical Society, (Burlington House, London, 1958 and No. 18, Supplement, 1965).

19. Witanowski, M., Tetrahedron, 23, 4299 (1967).

20. Witanowski, M., J. Am. Chem. Soc., 90, 5683 (1968).

21. In addition to McEwen's semiempirical method (Reference 11) involving self-consistent π-orbitals combined with a Hückel type σ system, Kato et al (H. Kato, L. Yonezawa, K. Morokum and K. Fukui, Bull. Chem. Soc., Japan, 37, 1710 (1964)) and Burnelle et. al. (L. Burnelle, P. Beaudouin, and L. Schaad, J. Phys. Chem., 72, 2240 (1967)) have applied extended Hückel calculations to the nitrite ion. Our CNDO molecular orbitals compare best with McEwen's orbitals. Also, the extended Hückel method gives a different ordering for the highest filled molecular orbitals; this is a common phenomenon of extended Hückel calculations (Reference 10 and references therein).

22. The ab initio calculations were completed using QCPE 104, "McLYOSH LINEAR MOLECULE PROGRAM I," A. D. McLean and M. Yoshimine. Dr. McLean's assistance is gratefully acknowledged.

23. Measurements on aqueous solutions of KCN were completed using a Cary 14 spectrophotometer. For previous mention of the CN^- absorption spectrum see R. P. Buck, S. Singhadeja, and L. B. Rogers, Anal. Chem., 26, 1240 (1954).

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720