Theoret. chim. Acta (Berl.) 5, 102—111 (1966)

The Electronic Structure of Tetra-Azapentalene

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Received January 21, 1966

The ultraviolet absorption spectra in various solvents and a study of the electronic structure of 1, 3a, 4, 6a-tetra-azapentalene are reported. The ASMO–SCF–CI method in the Pariser-Parr-Pople approximation has been used with different alternatives for evaluating the γ_{pq} and the $(A:pp)$ integrals. Only two out of the six different set of calculations have given an acceptable prediction of the first $\pi^* \leftarrow \pi$ transition; moreover the introduction of penetration integrals is found necessary for a correct prediction of the sequence of the N–N bond lengths based on the sequence of the bond orders.

Les spectres d'absorption ultraviolet dans des differents solvents et un étude sur la structure électronique du 1, 3a, 4, 6a-tetra-azapentalene sont exposés. La méthode ASMO–SCF–CI dans l'approximation de Pariser-Parr-Pople, a été employée avec plusieures alternatives pour le calcul des integrales γ_{pq} et $(A:pp)$. Entre les six differents calculs accomplis, deux seulement ont donné une prédiction acceptable pour la prémière transition $\pi^* \leftarrow \pi$. On a trouvé que pour une correcte prédiction de la séquence des longueures N–N sur la base des indices de liaison il faut introduir dans les calculs les integrales de pénetration.

Die UV-Absorptionsspektren von 1, 3a, 4, 6a-Tetraazapentalen in verschiedenen Lösungsmitteln werden angegeben. Die Elektronenstruktur dieser Verbindung wurde mittels SCF–CI-Rechnungen mit den Näherungen von Pariser-Parr-Pople und verschiedenen Sätzen von γ_{pq} und $(A:pp)$-Integralen ermittelt, wobei zwei der sechs Sätze einen annehmbaren π–π^*-Übergang liefern. Sollen sich die Werte der N-N-Bindungsordnungen in Übereinstimmung mit den entsprechenden Bindungslängen ergeben, so können die Durchdringungsintegrale nicht vernachlässigt werden.

Introduction

Tetra-azapentalene I, a new two-ring aromatic system, was identified by one of us with other co-workers [*1*] through the X-ray analysis of certain products prepared by PFLEGER, REINHARDT and HAHN [*15*], who had originally assigned to them the structure of 1, 2, 5, 6-tetra-aza-cyclo-octatetraene*. These compounds show typical aromatic properties, e.g. undergoing bromine substitution [*16*] and forming mono- and di-nitro derivatives which can be reduced to the corresponding amino-compounds and then diazotized [*17*].

The planar 1, 3a, 4, 6a-tetra-azapentalene ring system belongs to the class of the so-called meso-ionic compounds, for which a purely covalent formula based on

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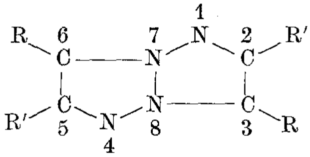
* Compounds supposed to have a similar structure had been obtained by METZE [*10*] and by CARBONI [*5*]; later the latter independently recognized them as tetra-azapentalene derivatives [*6*].

classical valency rules cannot be written, unless one denotes the N(7) and N(8) atoms by the classical notation $-\mathrm{N}{<}$ for the nitro group.

The meaning of the above notation and its use in representing the N($tr\,tr\,tr\pi^2$, V_3) valence state of nitrogen has been discussed recently by one of us [*13*] according to which the classical formula of tetra-azapentalene should be II.



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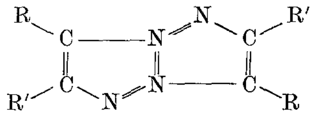

II

The valence state of N(1) and N(4) in I is N ($tr^2\,tr\,tr\,\pi$, V_2), and tetra-azapentalene is, therefore, a 10 π-electron aromatic structure, analogous to naphthalene or, even more so, to pyrido-(4, 3b)-pyridine (2, 6-naphthyridine), in which the 4 π-electrons of the C=C–C=C chain have been "squeezed" into the two central N–N atoms.

All these characteristics and the availability of molecular structure data for various terms of the series [*2, 3, 4*], made tetra-azapentalene an interesting example for testing the accuracy of predictions on the electronic spectra of this type of molecules with the approximate procedures used for analyzing the electronic structure of conjugated molecules. In the present paper a report of this work is presented.

The Ultraviolet Spectra

The ultraviolet absorption spectra, in various solvents, of three of the simplest substituted tetra-azapentalenes made available to us by Prof. PFLEGER were measured with a recording Cary Spectrophotometer. The relevant numerical data are given in Tab. 1 and some of the recorded spectra are shown in Fig. 1 and 2.

In all cases the protonic solvent causes a small low-energy shift of the first absorption band and a somewhat larger high-energy shift of the second band. The intensity and the nature of the shift leave no doubt as to the assignment of the first band to a $\pi^* \leftarrow \pi$ transition at about 4.5 eV. The most likely assignment for the second band appears to a $\pi^* \leftarrow n$ transition at $\simeq$ 5 eV. Its actual molar ε coefficient should be smaller than the recorded value shown in the table because

Table 1. *Absorption maxima of some tetra-azapentalene derivatives*

Compound	R	R'	Solvent	1st maximum cm^{-1}	1st maximum $10^{-4}\,\varepsilon$	2nd maximum cm^{-1}	2nd maximum $10^{-4}\,\varepsilon$
III	H	CH_3	*n*-hexane	36200	1.35	39500	0.68
			methanol	35800	1.50	40600	0.43
IV	Br	CH_3	cyclohexane	34800	1.50	40300	0.84
			ethanol-95	34600	1.40	40500	0.72
V	J	CH_3	cyclohexane	34800	1.65	38500	1.50
			n-heptane	34900	1.55	38500	1.45
			ethanol-95	34400	1.40	39200	1.10

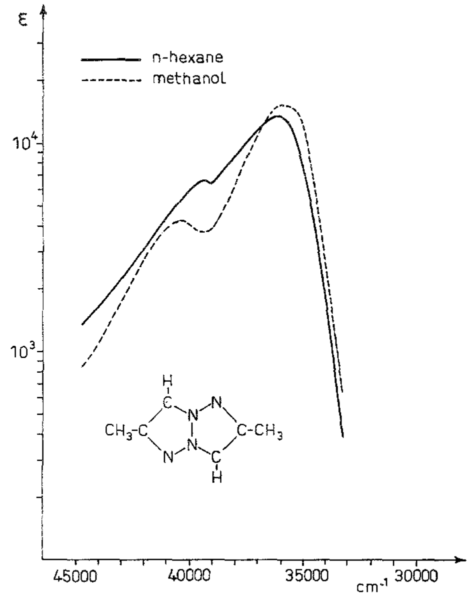

Fig. 1

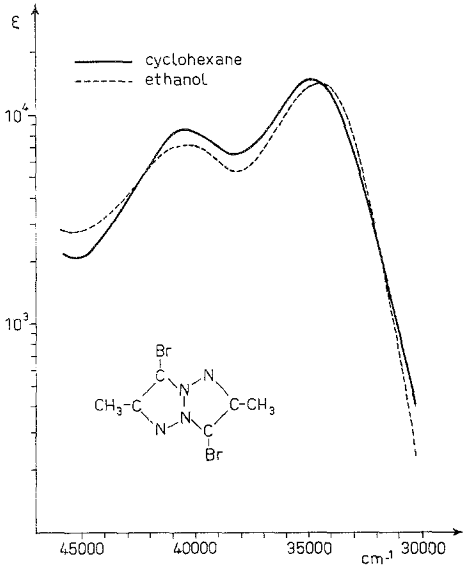

Fig. 2

Fig. 1. Absorption spectrum of 2.5-dimethyl-tetra-azapentalene in *n*-hexane and in methanol

Fig. 2. Absorption spectrum of 2.5-dimethyl-3.6-dibromo-tetra-azapentalene in cyclo-hexane and in 95%-ethanol

the band certainly overlaps the tail of the strong first $\pi^* \leftarrow \pi$. Moreover it is possible that a second $\pi^* \leftarrow \pi$ transition in this region overlaps the $\pi^* \leftarrow n$ band. The presence of the $\pi^* \leftarrow n$ on the high-energy side of the $\pi^* \leftarrow \pi$ transition is a peculiar characteristic of the observed absorption spectrum, since it is more common to find the reverse with the azasubstituted aromatic rings.

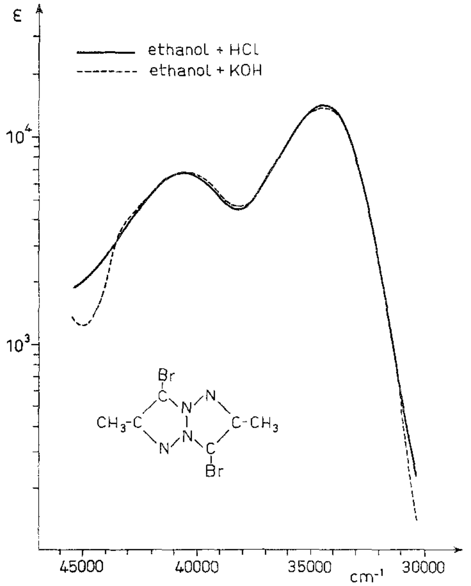

Fig. 3. Absorption spectrum of 2.5-dimethyl-3.6-dibromo-tetra-azapentalene in 0.04 *N* HCl and 0.04 *N* KOH in ethanol-water (4:1)

In order to ascertain to what extent the non-bonding lone pair electrons of the pyridine-like nitrogen, N(1) and N(4), conferred a basic character on the molecule, the absorption spectra of IV and V were recorded in acidic and alkaline hydro-alcoholic solutions. In both cases, there is almost no change from the absorption recorded in the neutral pure alcohol solvent (Fig. 3), showing, therefore, that the nitrogen atom lone pairs are far more strongly bound in tetra-azapentalene than they are in pyridine, for instance.

The π-Electron Distribution and Energy Levels

The study of the electronic structure of tetra-azapentalene was carried out according to the antisymmetrized molecular orbital procedure developed for π-electron systems by Pariser, Parr and Pople (PPP). The general outline of the theory is available in standard text books [*14*] and will not be given here.

The problem involves ten π-electrons on eight centers, whose core potential, shown in Fig. 4, belongs to the C_{2h} point group symmetry.

The calculations were carried out in two steps. Ground state molecular orbitals, self-consistent for the π-electrons were obtained first. Then a limited configuration interaction was carried out to obtain a reasonable approximation of the first excited levels of the molecule. The bond angles and distances were taken from the tridimensional refinement of the structure of the rubidium salt of 2, 5-dicarboxylic acid [*3*] and are shown in Fig. 4.

The PPP procedure can be applied using slightly different alternatives for the approximation implied in the method. Tetra-azapentalene, with its definite structure and available spectral data offered a good possibility of testing the merits of some of these alternatives.

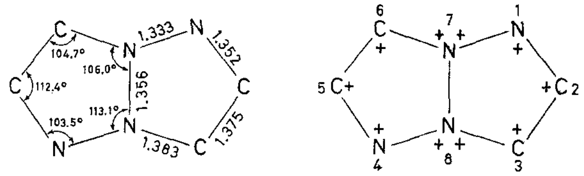

Fig. 4. Molecular core and dimensions of tetra-azapentalene

The first step the calculation was the choice of the valence state energies for the core atoms. The necessary data, taken from the recent work of Hinze and Jaffé [*8*], were:

$$W(C^+) = -11.16, \quad W(N^+) = -14.12, \quad W(N^{++}) = -28.72 \text{ eV}.$$

The β_{pq}^{core} integrals were then obtained from the formula

$$\beta_{pq} = \tfrac{1}{2} S_{pq} (W_p + W_q) \tag{1}$$

where S_{pq} is the overlap integral between the $2p\pi$ atomic orbitals of the adjacent atoms p and q.

The one-center coulomb repulsion integrals were taken as the difference between the valence state ionization potential and electron affinity

$$\gamma_{pp} = -W_p - A_p \tag{2}$$

using the numerical data already quoted [*8*] and the procedure described in a previous paper [*12*]. Referring to the scheme in Fig. 4 we have:

$$\gamma_{11} = 12.34, \quad \gamma_{22} = 11.13, \quad \gamma_{77} = 16.76 \text{ eV}.$$

Two alternatives have been used for evaluating the two-center coulomb repulsion integrals:

a) for interatomic distances where $R > 2.8$ A the exact value is taken; for distances where $R < 2.8$ A the formula originally proposed by Pariser and Parr was adopted [*14*]

$$\gamma_{pq} = \tfrac{1}{2}\,(\gamma_{pp} + \gamma_{qq}) - \lambda R - \mu R^2 \qquad (3)$$

where λ and μ are determined by fitting a parabolic curve to the exact theoretical values for $R = 2.8$ A and $R = 3.7$ A.

b) the formula proposed by Nishimoto and Mataga [*11*] was used

$$\gamma_{pq} = 14.397/(R + a), \qquad a = 14.397/\tfrac{1}{2}\,(\gamma_{pp} + \gamma_{qq})\,. \qquad (4)$$

In both formulas R is in Å and the integrals are in eV.

Table 2. α^{core} *integrals with the different choices for* γ_{pq} *and* $(A:pp)$

γ_{pq}	$(A:pp)$	α_1	α_2	α_3	α_7
PP	Neglected	−71.47	−63.56	−66.92	−93.30
	SS	−73.49	−65.55	−68.81	−93.05
	N.A.R.	−73.85	−67.10	−69.99	−95.33
NM	Neglected	−55.02	−49.00	−51.04	−71.86
	SS	−57.04	−50.98	−52.93	−74.61
	N.A.R.	−57.40	−52.53	−54.12	−76.89

Finally, the penetration integrals have been calculated by two different procedures:

a) using the interpolation formulae of Scrocco and Salvetti [*19*], based on the average spherosymmetric charge distribution implied in the Goeppert-Mayer and Sklar neutral atom potential operator;

b) by expressing the neutral atom potential operator as a combination of nuclear attraction and electronic repulsion terms [*9, 20*] in order to take into account the trigonal hybridization of the atomic σ-bond orbitals. This procedure, referred to as "N.A.R." (Nuclear Attraction and Repulsion) will be discussed in a following paper [*7*].

Table 3. *Calculated energy for the three lower* $\pi^* \leftarrow \pi$ $(B_u \leftarrow A_g)$ *electronic transitions*

γ_{pq}	$(A:pp)$	Singlets			Triplets		
PP	Neglected	5.68	6.43	8.12	4.12	5.45	5.55
	SS	5.49	6.29	8.09	3.75	5.32	5.47
	N.A.R.	5.22	5.81	7.94	3.06	4.77	5.67
NM	Neglected	5.11	6.01	7.65	2.75	4.32	5.14
	SS	4.96	5.91	7.57	2.45	4.25	5.05
	N.A.R.	4.83	5.46	7.53	1.92	3.81	5.33

The basic integrals, obtained as described above, are collected in the appendix.

Because the expression of the α^{core} integrals combines the γ_{pq} and the $(A:pp)$ integrals, six different evaluations are possible, according to the following scheme:

$$\begin{array}{l c l}
\gamma_{pq} & & (A:pp) \\
\left.\begin{array}{l}\text{Pariser-Parr (PP), Eq. (3);} \\ \text{Nishimoto-Mataga (NM), Eq. (4);}\end{array}\right\} & \begin{array}{c}\text{for each} \\ \text{one}\end{array} & \left\{\begin{array}{l}\text{neglecting them;} \\ \text{Scrocco-Salvetti (SS);} \\ \text{N.A.R.}\end{array}\right.
\end{array}$$

As a result, we have made six different calculations for S.C.F. π-MO electron distribution and energy levels of tetra-azapentalene, one for each set of α^{core} integrals listed in Tab. 2.

Before discussing the results, a few comments on the α values are appropriate. The α's obtained using the penetration integrals calculated according to SS are slightly lower than those obtained by the more elaborate N.A.R. procedure. Variations are between 1 and 2 eV, with the sole exception of α_1 which remains almost equal and as a result becomes differently scaled with respect to the others.

The α's from the NM repulsion integrals are lower, by over 20%, than those from the PP.

The results obtained for the $\pi^* \leftarrow \pi$ electronic transitions are shown in Tab. 3, and the S.C.F. π-charge distributions are shown in Tab. 4. A more complete tabulation of eigenvalues and eigenvectors is given in the appendix.

Table 4. *Calculated π-electron distribution*

γ_{pq}	$(A:pp)$	$q_1 = q_4$	$q_7 = q_8$	$q_2 = q_5$	$q_3 = q_6$
PP	Neglected	1.464	1.400	0.902	1.233
	SS	1.452	1.436	0.907	1.204
	N.A.R.	1.347	1.504	0.983	1.165
NM	Neglected	1.369	1.511	0.979	1.140
	SS	1.361	1.544	0.980	1.116
	N.A.R.	1.268	1.600	1.039	1.093

Discussion of the Results and Conclusion

The comparison of our results with the spectral measurement shows that the "best" calculated value for the lowest electronic transition ${}^1B_u \leftarrow {}^1A_g$ is 4.8 eV, about 0.3 eV higher than the observed transition. This agreement is not as "good" as that usually obtained with aromatic hydrocarbons, but it can be accepted as a "fair" one.

Had we carried out only this one good calculation, we could have explained the 0.3 eV difference by the fact that our spectra were measured on the dimethyl derivative of tetra-azapentalene, and, therefore, the observed transition should be augmented by a (assumed) red-shift induced by the substitution.

However, the data given in Tab. 3 show that only two out of the six different approaches have given acceptable results. We think that the most significant aspect of our work is, therefore, that it points out some of the inadequacies of the semiempirical π-electron S.C.F. procedure, as it is commonly applied to this type of molecules.

Hence, we cannot assess to what extent our spectral predictions are valid. With this reservation, we expect a second ${}^1B_u \leftarrow {}^1A_g$ transition at about 5.5—5.8 eV (which in our spectra might be overlapped with the transition provisionally assigned $\pi^* \leftarrow n$), and two ${}^3B_u \leftarrow {}^1A_g$ transitions near 2 and 4 eV, which should also appear in the emission spectra of the molecule.

On examining all the results of Tab. 3, a fairly regular trend becomes apparent as one proceeds form one approach to the next. The PP γ_{pq} integrals lead to higher transitions than the NM integrals. The introduction of the penetration integrals lowers the calculated transitions whatever technique is used for their computation.

Judging by the electronic transitions, we would conclude that the N.A.R. and the SS procedures are almost equivalent and that the latter being the simplest, should be the preferred one. This conclusion, however, is not supported by a closer scrutiny of the wave-functions and density matrix elements obtained in the different calculations.

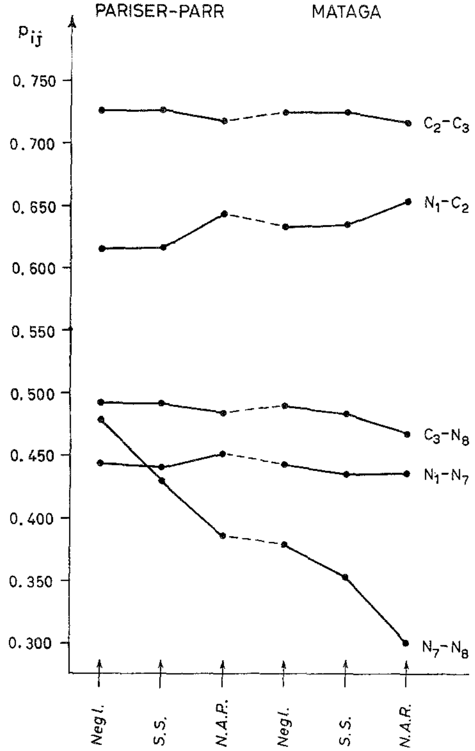

Fig. 5. Bond orders for tetra-azapentalene calculated using the Pariser-Parr (PP) and Nishimoto-Mataga (NM) alternatives for γ_{pq}, when the penetration integrals are either neglected (Negl.) or obtained by the Scrocco-Salvetti (SS) and the N.A.R. procedures

From the π-electron distribution shown in Tab. 4 we can see that using the N.A.R. procedure there is a reduction* of about 0.1 e in the π-orbital population of N(1) and N(4). The electron population removed from them is mainly distributed among N(7), N(8), and C(2), C(5) so that the carbon net-charge which results is opposite in sign to that obtained by all the other approaches.

It is difficult to say whether this marked change in the π-electron density distribution is significant or not. The following consideration would suggest that it is. As already observed when discussing the spectra, the $\pi^* \leftarrow n$ transition of tetra-azapentalene has a higher energy than the $\pi^* \leftarrow \pi$ (this is true whatever the assignment of our second observed transition, because no absorption having a $\pi^* \leftarrow n$ character is observed of lower energy than 4.5 eV). This means that the so-called non bonding electrons do occupy a molecular orbital whose level should be about 0.5 eV lower than the highest occupied π-electron molecular orbital. There is, therefore, a strong polarization of the n-electrons and it is likely that the net S.C.F. π-population represents only a rough approximation of the N(1) and N(4) net charge. This should be balanced by a shift of the n-population which affects, in turn, the bond lengths and the basicity of the molecule.

Other evidence for the role played by the penetration integrals in the present calculations comes form the π-bond orders p_{ij} calculated from the different S.C.F. wave functions and compared in Fig. 5.

The C–C bond order is apparently not affected by the different ways of calcu-

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* This is due to the situation, as already mentioned, in which the scaling of the α_1 core integral relative to the others is markedly changed when the N.A.R. procedure is used. The point of interest here is that the variations in the α's, and the consequent changes in q_i and p_{ij} come from a more correct evaluation of the π and lone pair electron interaction.

lating γ_{pq} and $(A:pp)$. Their effect on the C–N bonds is moderate and in each case the longest C(3)—N(8) bond shows correctly a lower index than the shorter C(2)—N(1).

The introduction of the penetration integrals, however, seems to be essential for agreement with the observed sequence of the N–N bond lengths, and the N.A.R. procedure appears the most suited at least when the PP γ_{pq} integrals are used.

The effect of the penetration integrals on the N(1) and N(4) π-electron population and on the N(7)—N(8) bond order is perhaps the most remarkable aspect of our results. Such an effect is the consequence of a limited interaction of the π-electrons with the core-electrons, and the N.A.R. procedure is certainly the more accurate of the two, because it takes into account the trigonal hybridization of the σ-orbitals and of their different electron population in the valence state of N(1) and N(4). Clearly this is not a consistant way of bringing in the σ-π interaction, but certainly it is right to introduce it, as a first approximation, because of its paramount significance in the core-terms.

Finally, an interesting comparison can be made between our "best" NM-N.A.R.-S.C.F. charges and bond orders and those obtained by POOLE [*18*] using the simplest conventional MO treatment.

Starting with the parameters $\alpha_1 = \alpha + 0.5\,\beta$, $\alpha_7 = \alpha + 1.5\,\beta$
$\beta_{\mathrm{NN}} = \beta_{\mathrm{CC}} = \beta$, $\beta_{\mathrm{CN}} = 0.8\,\beta$, he finds: $q_1 = 1.395$, $q_2 = 1.046$, $q_3 = 1.085$,
$q_7 = 1.474$, $p_{23} = 0.754$, $p_{12} = 0.587$, $p_{38} = 0.495$, $p_{17} = 0.462$, $p_{78} = 0.397$.
The carbon atoms have the same polarities as in the best S.C.F. calculations and the sequence of the bond orders corresponds to the observed bond lengths. This much simpler procedure gives a ground state picture of our molecule which is definitely better than that obtained by some of the more sophisticated approaches.

Our application of the PPP-S.C.F. A.S.M.O. method to tetra-azapentalene, therefore, seems to indicate that:

a) the introduction of penetration integrals is necessary for a nearly correct prediction of the lowest singlet-singlet transition on molecules of this type;

b) the two procedures used for the penetration integrals are almost equivalent for predicting the electronic transitions, but the N.A.R. procedure seems more adequate for predicting the correct sequence of the bond lengths when these are related to the π-bond orders;

c) although the NM γ_{pq} integrals have given a better agreement with the measured electronic transition and the observed bond length sequence, a definite choice between them and the PP formulae for γ_{pq} requires a more detailed analysis of the influence of other factors, such as configuration interaction.

The general validity of these findings cannot be assessed from a single example and a more extensive test of the technique is necessary before drawing any conclusion. Work along these lines will be described in a following publication [*7*].

Aknowledgments: The calculations were carried out on the IBM 7040 computer of the Istituto Superiore di Sanità, using the program developed in the Quantum Chemistry Laboratory at the Illinois Institute of Technology and kindly made available to us by Prof. P. G. LYKOS.

The authors are grateful to Dr. M. CIGNITTI for several discussions and for help in the computations.

The work was carried out with the financial support of the Italian National Research Council (C.N.R.).

Appendix

Evaluation of integrals

The orbital exponents for the core atom $2p\pi$ A.O.'s were as follows:

$$C^{+}: 3.25 \qquad N^{+}: 3.90 \qquad N^{++}: 4.25\,.$$

The penetration integrals $(A{:}pp)$ have been calculated using as Z_A for neutral atoms: 2.90 for C and 3.55 for N; as Z_p for the core A.O., those above. The overlap integrals are: $S_{12} = 0.2071$, $S_{17} = 0.1516$, $S_{23} = 0.2548$, $S_{38} = 0.1717$, $S_{78} = 0.1256$.

The two center repulsion integrals and the penetration integrals are given in Tab. A-1 and A-2.

Table A.1
Two-center coulomb repulsion integrals γ_{pq} (eV)

pq	PP	NM
12	7.846	5.583
13	5.846	4.111
14	4.121	3.115
15	4.091	3.027
16	5.335	3.802
17	8.898	6.199
18	6.159	4.431
23	7.601	5.395
25	3.490	2.679
26	4.023	3.010
27	6.442	4.596
28	6.235	4.475
37	6.249	4.482
38	8.482	5.960
78	9.559	6.500

Table A.2.
Penetration integrals (eV)*

$(A{:}pp)$	SS	N.A.R.
1:22	0.679	1.895
1:33	0.011	0.806
1:55	0.002	0.228
1:66	0.003	0.206
1:77	0.597	2.066
1:88	0.005	0.835
2:11	1.305	1.192
2:33	1.258	1.109
2:77	0.094	0.052
2:88	0.068	0.036
3:11	0.032	0.027
3:44	0.009	0.008
3:77	0.069	0.037
3:88	1.375	1.042
7:11	0.631	1.011
7:22	0.262	0.163
7:33	0.018	0.145
7:44	0.007	0.140
7:55	0.017	0.144
7:66	0.600	0.810
7:88	0.537	0.958

* Penetration integrals less than 0.005 eV in both approaches are not given.

Numerical results for eigenfunctions and eigenvalues

The two sets of results reported are those obtained using N.A.R. penetration integrals with the PP and the NM γ_{pq} integrals. All the other data can be made available upon request to the authors. The self-consistency in M.O. coefficients is up to 10^{-4}.

If we write the symmetry atomic orbitals in the matrices $\chi(\Gamma)$:

$$\chi(A_u) = \{(\chi_1 + \chi_4) \quad (\chi_2 + \chi_5) \quad (\chi_3 + \chi_6) \quad (\chi_7 + \chi_8)\}$$
$$\chi(B_g) = \{(\chi_1 - \chi_4) \quad (\chi_2 - \chi_5) \quad (\chi_3 - \chi_6) \quad (\chi_7 - \chi_8)\}$$

and define the one-column matrices of the coefficients C_n, the M.O. $\psi_n(\Gamma)$ are given by

$$\psi_n(\Gamma) = \chi(\Gamma)\, C_n\,.$$

The M.O. are in the order:

$$\psi_1(A_u),\quad \psi_2(B_g),\quad \psi_3(B_g),\quad \psi_4(A_u),\quad \psi_5(A_u),\quad \psi_6(B_g),\quad \psi_7(B_g),\quad \psi_8(A_u)\,.$$

The NM – N.A.R. C_n matrices and eigenvalues are:

n:	1	2	3	4	5	6	7	8
	0.197	0.311	−0.374	0.329	−0.501	−0.480	0.182	−0.320
	0.083	0.001	−0.479	0.525	0.085	0.189	−0.484	0.458
	0.190	−0.282	−0.361	0.243	0.492	0.274	0.464	−0.404
	0.647	0.569	0.026	−0.238	−0.003	0.398	0.131	0.157
ε_n:	−25.78	−19.59	−16.30	−14.75	−11.80	−4.30	−2.98	−2.03

The PP – N.A.R. corresponding results are:

n:	1	2	3	4	5	6	7	8
	0.221	0.364	0.370	0.345	−0.486	−0.468	0.107	−0.310
	0.096	0.013	0.462	0.508	0.105	0.268	−0.463	0.470
	0.208	−0.300	0.384	0.221	0.503	0.181	0.479	−0.394
	0.631	0.527	−0.048	−0.271	−0.011	0.420	0.210	0.166
ε_n:	−26.88	−20.64	−18.12	−16.12	−13.54	−3.49	−2.44	−1.37

The configuration interaction treatment was carried out with the following mono-excited configurations: $\psi_4 \to \psi_6$; $\psi_4 \to \psi_7$; $\psi_5 \to \psi_6$; $\psi_5 \to \psi_7$, all of which belong to the B_u representation of C_{2h}.

The configuration interaction matrix elements for the NM – N.A.R. and the PP – N.A.R. alternatives can be obtained by known procedures [14] from the data given above.

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