Quantum Chemical Predictions Concerning Two Unknown "Mesoionic" Compounds.

Leonello Paoloni (1) and Antonio Ciampi.

Istituto Superiore di Sanità, Laboratories of Chemistry and Gruppo di Chimica Teorica del C.N.R.

The Pariser-Parr-Pople approximation was used to predict the properties of compounds I, 3-oxo-2*H*-1,2,3-triazolo[3,4-*a*]pyridine, and II, 3-oxoisoxazolo[2,3-*a*]pyridine, originated by joining a pyridine ring to two sydnone-like heterocyclic systems not yet reported in the literature. A parallel computation was carried out for two known compounds of similar structure, to give the predictions a better reliability through the comparison with observed spectral data and chemical behaviour. Compound I is expected to be stable, with an absorption spectrum similar to III, 2-oxo-1,3,4-oxadiazolo[4,5-*a*]pyridine, and chemical properties analogous to IV, 1-methyl-3-oxo-1,2,4-triazolo-[4,3-*a*]pyridine. A reaction path is suggested for obtaining from I the unknown isomeric structure V, 3-oxo-1*H*-1,2,3-triazolo[3,4-*a*]pyridine. Compound II is predicted as an unstable orange-red substance which should be handled and kept at low temperatures.

Various heterocyclic systems related to sydnone and formed by combining carbon with nitrogen and oxygen atoms, each in a suitable chosen valence state, were studied in a previous paper (2) using the simplest approximation of the molecular orbital (MO) method. Several of these systems represented new structures, in the sense that the corresponding compounds have never been described in the literature, neither as substituted derivatives, nor as parts of larger condensed ring systems. A comparison of the calculated properties of the known compounds with those of the unknown ones suggested that the existence of all of them was equally possible.

The approximations involved in the calculations summarized above (2) prevented reasonable predictions being made of the chemical and spectroscopic properties of the unknown compounds. The purpose of the present paper is to report on the more elaborate calculations that have been carried out on two of the unknown compounds previously considered (3) and on two other compounds of comparable structure already described in the literature, using the Pariser-Parr-Pople approximation of the ASMO, SCF, CI method. In this way the predictions made about the existence of certain compounds and their chemical and spectroscopic properties can be given a larger measure of reliability, for they are based on a better approximation than that used before (2) and are also based on a parallel comparison with the properties of known compounds.

Results and Discussion.

The molecules studied in this paper are shown in Figure 1. They were all assumed to be planar, and the interatomic distances and angles were average values of those of molecules of similar structure (4).

The oxo-substituted penta-atomic heteroaromatic rings of I and II are related, respectively, to triazolone and isoxazolone, but the atomic valence states are differently arranged, and therefore correspond to unknown systems of 8 π-electrons analogous to sydnone. The electronic structure of the molecules shown in Figure 1 is built up from 12 π-electrons over 10 centres, and it is obvious that many other compounds can be constructed having the same heteroaromatic rings as I and II embodied in their structures. These two examples were studied because it should be possible to start their synthesis with compounds which have the desired valence states for the nitrogen and carbon atoms in the common bond of the two condensed rings.

Molecules I and II seem to be unknown so far (3), whereas III has been obtained by Hoegerle (6) and IV has been obtained by Palazzo and Baiocchi (7).

The details of the method of calculation that was used are not given here because they have been already described in other papers (8). The basic integrals and other relevant data are tabulated in the Experimental Section.

The problem of the existence and stability of I and II was resolved by examining the π-electron energy in the molecule and the energy of the same electrons in the free atoms, in their assigned valence states. One can write:

$$\Delta E_\pi = \sum_i (I_i + \epsilon_i) - \sum_p n_p W_p ,$$

where ϵ_i is the eigenvalue of the ψ_i molecular orbital, $I_i = (\psi_i/H/\psi_i)$ and the i^{th} summation is carried out over

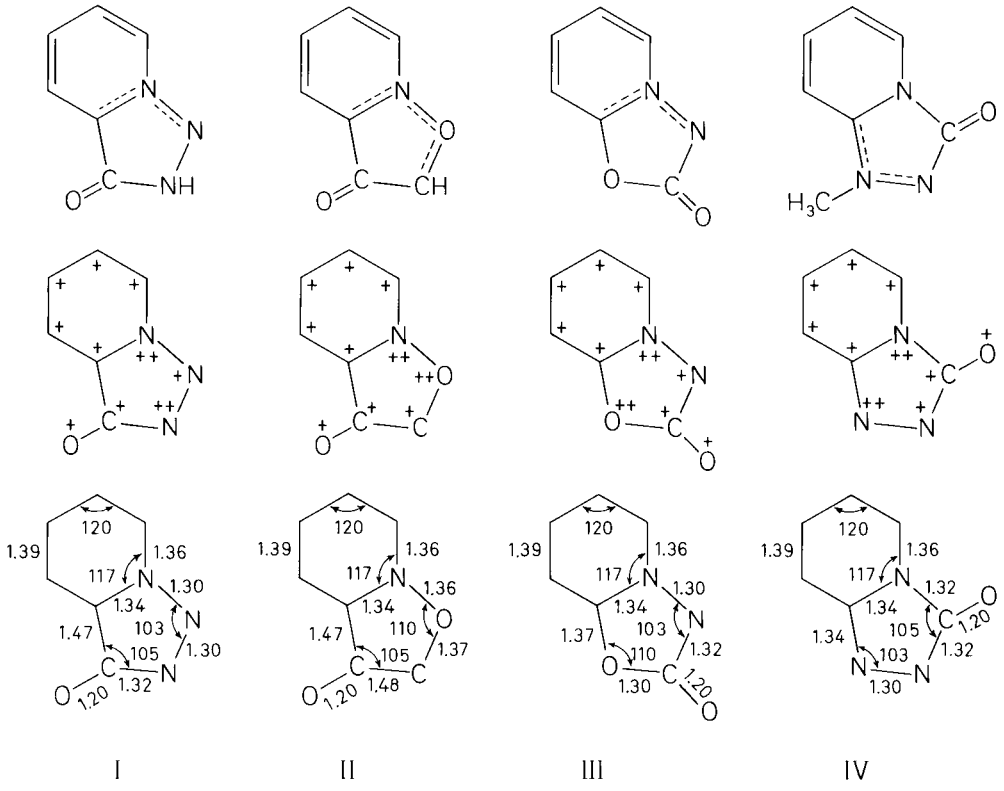


Fig. 1. Formulae (a), π-electron cores and molecular dimensions for the compounds: I, 3-oxo-2*H*-1,2,3-triazolo-[3,4-*a*]pyridine; II, 3-oxoisoxazolo[2,3-*a*]pyridine; III, 2-oxo-1,3,4-oxadiazolo[4,5-*a*]pyridine; IV, 1-methyl-3-oxo-1,2,4-triazolo[4,3-*a*]pyridine. The C-C bonds of the pyridine ring were all assigned the same length 1.39 Å.

(a) These formulae differ from those used in reference 3 for the same compounds. The valence state symbolic representation there adopted was discussed before (5) and was shown to allow a coherent extention for writing the classical formulae. This is mentioned here because the compounds I, II and V were found out through the systematic development of the valence state interpretation of the classical notation. The correlation of the symbols -N<, -N=, -O-, O=, etc., with the valence states N($tr\ tr\ tr\ \pi^2$, V_3), N($tr^2\ tr\ tr\ \pi$, V_2), O($tr^2\ tr\ tr\ \pi^2$, V_2), O($tr^2\ tr^2 tr\ \pi$, V_1) adequately reflects the electronic structure of the molecules and shows that the so-called "mesoionic" compounds do not require a special notation. All that needs to be shown in the formula is the *n*-coordination index of the valence state V_n, and this is more commonly done by writing e.g. the aromatic ring as an hexagon with an enclosed circle (13), or by using dashed bonds, as done here. This is enough to represent the space arrangement of the atoms and the existence of a certain degree of electron delocalization. The remaining quantitative aspects of the electron distribution are then left to the calculated molecular diagram, or to the ground state wave function.

the MO's occupied in the ground state; W_p is the valence state ionization potential of the atom *p* which contributes n_p π-electrons to the molecule, and the *p* summation is carried out over all the atoms of the molecule. The calculated ΔE_π were (in eV):

(I) : -412.83 ; (II) : -399.44 ; (III) : -420.33 ; (IV) : -412.43.

The molecular core corresponding to III therefore receives the largest energy gain; I is about the same as IV, and II is the less favoured of the group, its gain being nearly 5% less than that of III. However, there are no grounds for doubting the existence of I and II, because the ΔE_π in both cases are large enough and of a comparable magnitude as those found for the known molecules III and IV.

Another insight into their stability can be obtained by considering the calculated excitation energy of the lowest triplet state, which is (eV):

(I) : 2.86 ; (II) : 0.74 ; (III) : 3.68 ; (IV) : 2.50.

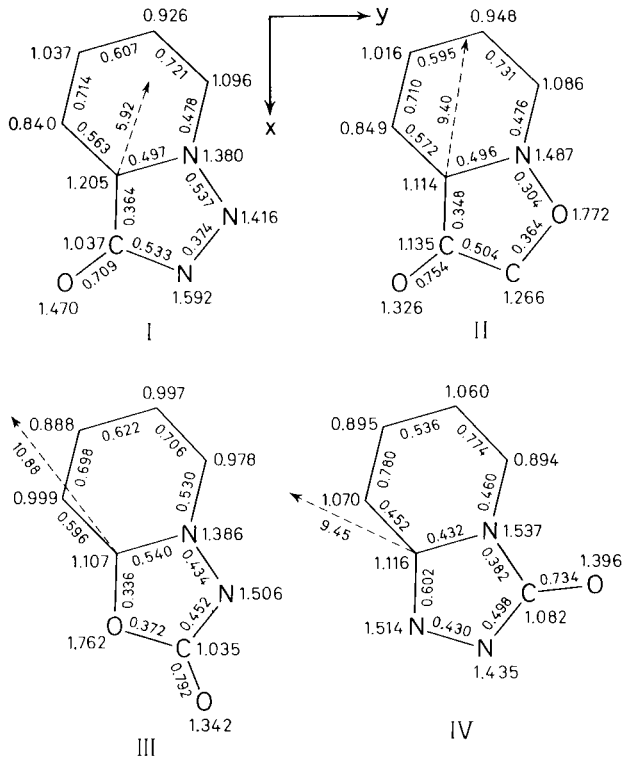


Fig. 2. Molecular diagrams, with π-electron distribution and the total dipole moment of the molecules I to IV. Details on the dipole moment calculation are given in the Experimental Section.

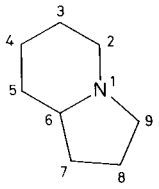
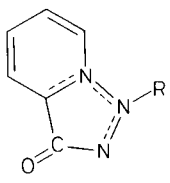


Fig. 3. Numbering of the atomic orbitals.



V

This sequence is coherent with that found above for ΔE_π. The lowest triplet of II, corresponding to energy absorption in the near infrared at about 1.7 μ, must be comparatively much more populated than that of the other molecules at the same temperature. Therefore a significant fraction of the molecules in II could reach, even at room temperature, a diradical state with the two unpaired π-electrons mainly distributed in the atomic orbitals 8, 10, 4 and 6, and start, or speed up, *inter-* or *intra-*molecular reactions ending in a more stable molecular configuration. Altogether II is predicted as being a structure which will be difficult to synthesize and whose stability will be favoured by keeping and handling it at low temperatures, whereas synthesizing and handling I should not be more difficult than for the known structures III and IV.

The ground state picture of the molecules which results from our calculation is given in Figure 2, where the π-electron distribution and the total dipole moment are shown. A feature common to all the molecules is the π-electron migration from the pyridine to the sydnone-like ring: the sum of the π-electron population of the external four carbon atom chain is about 3.9 *e* in all cases. This circumstance, and the strong charge polarization typical of sydnone-like structures, give rise to the large value of the total dipole moment, the direction of which, (-) → (+), is always close to the line from the oxygen of the carbonyl group to the centroid of the pyridine ring. If the charge density on each carbon atom of the pyridine ring is taken as a measure of the possibility of an electrophilic attack, then the results would suggest that I and II could be preferentially substituted in α and γ, whilst IV could be substituted in β and δ of the pyridine nitrogen. Taking the data at their face value III should be less liable to electrophilic attack and show a definite nucleophilic preference at the γ position (9). We have been unable to find data in the literature on III and IV to compare with these predictions.

Bond cleavage reactions have been described (6) (7) both for III and IV, but the mechanism is uncertain and does not help in making useful predictions about I and II. The formation of quaternary ammonium derivatives of IV has shown an interesting feature (10) for quaternization with methyl iodide occurs on nitrogen *2*, as expected, but the thermal decomposition of the salt eliminates the alkyl group on nitrogen *1*. It is very likely that a similar sequence of reactions could take place with I, ending in a product V, 3-oxo-1*H*-1,2,3-triazolo[3,4-*a*]pyridine, not yet described in the literature, which is equally possible in terms of the valence states of the constituent atoms. It is not possible to state at the present time whether V is favoured with respect to I. If this is not the case, then the quarternization and decomposition sequence should go in the opposite direction, and I would be obtained from V (11).

To the extent that the packing in the crystal lattice is controlled by dipole-dipole interaction, all the molecules

considered here should show similar melting points and similar solubilities. This can be verified for III and IV, which melt at 225 and 216° respectively, and which dissolved unchanged in a variety of polar solvents and hydrocarbons (6) (7). Melting of II without decomposition seems unlikely, as discussed before; a lower melting point for I is possible because its dipole moment is considerably lower than that of III and IV.

The last prediction concerns the "color" of I and II. The calculated electronic transitions were compared with the absorption spectrum of the molecules and the data are collected in Table I. The measure of agreement with the observed spectrum (12) is within the usual approximation of the method (8) for IV, and is somewhat worse for III. Considering however, that the molecular geometry is only based on average bond lengths and angles, the general

TABLE I

Lowest Electronic Transitions, eV.

	I	II	III		IV	
	calcd.	calcd.	calcd.	obs. (a)	calcd.	obs. (a)
1st	4.30	2.69	4.73	4.21	3.84	3.66
2nd	4.81	2.86	4.90	4.76	4.66	4.45

(a) In ethanol as the solvent. See references 6,7 and 12.

TABLE A-I

Overlap Integrals for the Bonds of the Penta-atomic Ring

Indexes	I	II	III	IV
6.7	0.216	0.216	0.138	0.188
7.8	0.197	0.212	0.161	0.163
8.9	0.166	0.138	0.223	0.223
9.1	0.166	0.095	0.163	0.195

TABLE A-II

Valence State Ionization Potentials W_p
and one Centre Coulomb Repulsion Integrals γ_{pp}, eV.

core atom	C^+	N^+	N^{++}	O^+	O^{++}
$-W_p$	11.16	14.12	28.72	17.70	34.12
γ_{pp}	11.13	12.34	16.76	15.23	18.82

pattern of the results is satisfactory and allows one to predict with confidence that the absorption of I should resemble that of III (bands at 297 and 262 mμ.) and II should show two absorption maxima at about 460 and 440 mμ (approximation ± 30 mμ) and appear as an orange or red substance.

In conclusion it should be stressed that one motive for this research was to see if any particular feature or molecular property could be related to the fact that a classical covalent formula cannot be written for certain molecules. So far no such feature has been found and it is to be hoped that the results presented here will stimulate attempts to synthesize the predicted compounds, a task which might not have been considered worthwhile in the past because some of the formulae satisfying the valence state rules (5) do not conform to the classical picture of covalent bonding.

EXPERIMENTAL

The outline of the method and the details about the calculation of the matrix elements are given in reference 8. That information is added here which is relevant to the molecules we have considered, and implies a certain degree of arbitrariness in its choice.

The numbering adopted for the atomic orbitals is shown in Figure 3 (for calculations only). The exocyclic oxygen atom a.o. was given always the index *10*.

The overlap integrals S_{ij} of the pyridine moiety are the same for all molecules, as follows (Slater a.o.): $S_{12} = 0.180$, $S_{23} = S_{34} = S_{45} = S_{56} = 0.248$; $S_{16} = 0.189$. The overlap integral for the C=O exocyclic bond is $S_{CO} = 0.228$. The other overlap integrals are given in table A-I. The parametric values of the valence state ionization potential W_p and the one-centre coulomb repulsion integral γ_{pp} of each core atom are listed in table A-II.

The β_{pq}-core integrals were calculated from the formula

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

The coulomb two-centre repulsion integrals γ_{pq} for distances $R > 2.8$ Å were calculated by the Roothaan integral expansion, whereas those over distances $R < 2.8$ Å were evaluated, as originally proposed by Pariser and Parr, by fitting the exact integral value at distance 2.8 and 3.7 Å with the formula:

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

The coefficients λ and μ (R in Å, and γ_{pq} in eV) are listed in table A-III for the various possible couples of core atoms.

The penetration integrals (A_q:pp) were calculated by expressing the neutral atom potential operator as a combination of nuclear attraction and electron repulsion terms, with the σ-frame assumed of purely trigonal hybrids. The direction of the extra-cyclic bonds was taken as bisecting the external angle, with the following bond lengths: C-H, 1.08; N-H, 1.00 and N-Me, 1.45 Å. The required attraction and repulsion integrals were evaluated from the Roothaan integral expansion, the exchange integrals were neglected.

The α_p-core integrals, obtained from the W_p, γ_{pq} and (A_q:pp), are listed in table A-IV.

The SCF iterations (up to 10^{-4} in the M.O. eigenvectors) and the Configuration Interaction calculations were finally carried out using the program developed by the Quantum Chemistry Laboratory at the Illinois Institute of Technology, Chicago, and kindly made available to us by Prof. P. G. Lykos.

The total dipole moment was calculated by addint the μ_π and μ_σ moments. The first was obtained from the net charge distribution derived from the molecular cores of Figure 1, and the π-electron distribution of Figure 2. The second was evaluated from the following bond moments (in D): (-)C-H(+), 0.4; (-)N-H(+), 1.3; (+)C-N(-), 0.45; (+)C-O(-), 0.8; (+)N-O(-), 0.5.

TABLE A-III

Coefficients λ and μ for γ_{pq} Integrals on Distances $R < 2.8$ Å

core atoms		λ	μ
C^+	C^+	2.9112	0.2518
C^+	N^+	3.2629	0.3036
C^+	N^{++}	4.6394	0.5145
C^+	O^+	4.1527	0.4390
C^+	O^{++}	5.2724	0.6108
N^+	N^{++}	4.9881	0.5655
N^{++}	N^{++}	6.3635	0.7761
N^{++}	O^+	5.8760	0.7005
N^{++}	O^{++}	6.9951	0.8720
O^+	O^{++}	6.5073	0.7963

TABLE A-IV

Value of the $-\alpha_p$-core

p	1	2	3	4	5	6	7	8	9	10
I	100.690	76.036	67.877	67.031	72.496	88.341	86.183	92.441	85.435	73.959
II	102.928	77.457	68.287	67.166	72.351	87.765	81.965	77.740	98.086	70.124
III	101.533	76.176	68.063	69.956	73.614	91.261	100.013	88.563	87.580	74.567
IV	101.627	76.018	67.859	67.225	73.545	90.633	91.359	84.517	86.748	73.561

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REFERENCES

(1) A preliminary report on this work was given by L.P. at a seminar held at the University of Göttingen in May 1966.

(2) L. Paoloni and A. G. Giumanini, *Gazz. Chim. Ital.*, 96, 291 (1966).

(3) See reference 2, p. 308: Structures 2.1 and 4.1 of Figure 8.

(4) L. E. Sutton, Ed., "Tables of Interatomic Distances", The Chemical Society, London, 1958, p. S 7, S 12 and ff; *idem.* Supplement, London, 1965, p. S 7s, S 14s and ff.

(5) L. Paoloni, *Gazz, Chim. Ital.*, 96, 83 (1966). See also the footnote of Figure 1 in the text.

(6) K. Hoegerle, *Helv. Chim. Acta*, 41, 548 (1958).

(7) G. Palazzo and L. Baiocchi, *Ann. Chim. (Rome)*, 55, 935 (1965).

(8) M. Cignitti and L. Paoloni, *Theoret. Chim. Acta (Berlin)*, 7, 383 (1967).

(9) The charge distribution on the carbon atoms α and γ to the pyridine nitrogen seems to correlate with the relative position of the carbonyl group.

(10) G. Palazzo and L. Baiocchi, *Ann. Chim. (Rome)*, 56, 190, 199 (1966), and also reference 7.

(11) The position of the N($tr\ tr\ tr\ \pi^2$, V_3) atoms relative to the carbonyl group in I is the same as that found in the so-called Besthorn-red (see F. Krollpfeiffer and K. Schneider, *Ann. Chem.*, 530, 34 (1937) and also W. Baker, in "Perspectives in Organic Chemistry", A. Todd, Ed., Interscience Publ. Inc., New York, 1956, p. 64). This circumstance indicates that there should be no formal objection to the possible existence of the bond arrangement proposed for I.

(12) Spectral data are from reference 6 for III and reference 7 for IV. Only the two lowest transitions have been taken into consideration and compared with the observed spectra, because of the limitations inherent in the calculations, where only the four lowest singly-excited configurations were introduced. A more extensive configuration interaction would have little meaning for molecules of unknown geometry.

(13) W. Baker, *Proc. Chem. Soc.*, 75 (1959).

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