CONFORMATIONAL PREFERENCES ABOUT C$_{py}$-S BONDS IN DI-2-PYRIDYL DISULFIDE

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ABSTRACT

The total energy, dipole moment and electron densities for each possible rotational conformation about the C_{py}—S bonds of di-2-pyridyl disulfide were evaluated by using the semi-quantitative CNDO/2 method. The conformations in which the pyridine rings are coplanar with the valency plane of the bonded sulfur atom (cis-cis, cis-trans and trans-trans) were predicted to be the most favored ones.

Results of the theoretical study, when compared to some experimental determinations such as dipole moment and variable temperature pmr spectra, provided evidence that easy interconversion between these conformations can occur.

Introduction

Although diaryl disulfides constitute an interesting part of biological, industrial, and coordination chemistry, as yet no attempt has been made to examine these systems in terms of molecular orbital theory.

Our recent interest on the conformational preferences about C_{ar}—S bonds of model diphenyl disulfide molecules prompted us to analyze theoretically the conformation of di-2-pyridyl disulfide by using CNDO/2 type approximate molecular orbital calculations. The aim of the present work is thus to study the influence of the angles of twist about the C_{py}—S bonds on the total energy of the investigated molecule. This paper also reports the pmr spectroscopic study of di-2-pyridyl disulfide at ambient and low temperatures together with the related electronic properties of this molecule. These measurements have been carried out to test the effectiveness of the semi-quantitative method in predicting the molecular solute conformation and reproducing some experimental data.

The results obtained are of interest in that they represent an extension of earlier work with more conventional techniques of dipole moment measurements.[1]

Method of Calculation

Calculations have been performed by application of the semiquantitative CNDO/2 all-valence electrons

method developed by Pople and Beveridge.[2] In this approach the $3d$ orbitals of sulfur have been included in the valence set.

The carbon-sulfur and sulfur-sulfur bond lengths adopted were those reported by X-ray diffraction study of diphenyl disulfide, i.e., 1.80 and 2.03 Å respectively.[3] The C–S–S–C dihedral angle and the C—S–S valency angles were assumed to be 96.2° and 106°, respectively, as in the case of crystalline diphenyl disulfide. The molecular geometries of the pyridine rings were approximated as regular hexagons. The ring bond lengths were fixed at the standard values of 1.40 Å, and all carbon-hydrogen bonds were taken as 1.08 Å. All bond lengths were assumed to be unchanged by the rotation about the C_{py}—S bonds.
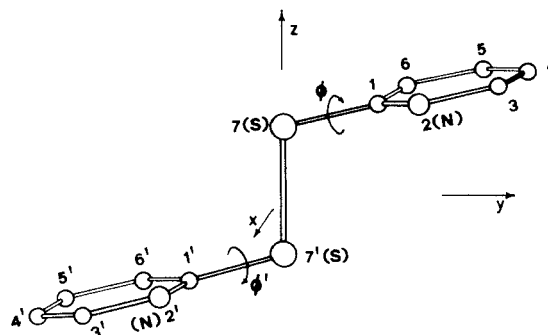

FIGURE I

Atom numbering scheme and reference axes for di-2-pyridyl disulfide. The molecule is presented in the conformation in which the rotation angles are (0°, 0°)

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The input data of the computer program was presented as atomic numbers and cartesian coordinates. The atomic numbering scheme and coordinate system used for the calculations are depicted in Figure I.

Results and Discussion

Theoretical Calculations

In our calculations the dihedral angle about the S—S bond was held fixed as the rotation angles about C_{py}—S bonds were varied from $0°$ to $360°$ with a scanning of $15°$. The complete map of isoenergy curves has then been drawn, describing the variation of the total energy resulting from the mutual rotation of the pyridine groups. This map (Figure II) was generated starting with a standard conformation, in which the pyridine ring planes are perpendicular to the C—S—S planes and the N atoms are positioned inside the C—S—S—C dihedral angle (see Figure I). As the two pyridine groups rotate about the C_{py}—S bonds—the

rotations ϕ and ϕ' occurring in the clockwise direction shown by the arrows in Figure I—the angle values (ϕ, ϕ') are used to designate the conformation so obtained.

The map in Figure II clearly shows that the conformations defined by the rotation angles $(90°, 90°)$, $(90°, 270°)$, $(270°, 90°)$, and $(270°, 270°)$ are the most stable ones. This would therefore indicate that the equilibrium conformations about the C_{py}—S bonds of di-2-pyridyl disulfide are such that the pyridine ring planes are coplanar with the sulfur valency planes, the N atoms being cis-cis-conformation $(270°, 270°)$-, trans-trans-conformation $(90°, 90°)$-, and cis-trans-conformation $(90°, 270°)$ or $(270°, 90°)$- with respect to the S—S linkage.

The minimum energy values and the calculated dipole moments are presented in Table I. It should be noted that the cis-cis-conformation which corresponds to the much lower minimum, is in accord with experimental dipole moment information on a similar compound, $i.e.$, methyl 2-pyridyl sulfide.[4]

It is also of interest to observe that interaction between the sulfur $3d$ orbitals and the p orbitals of
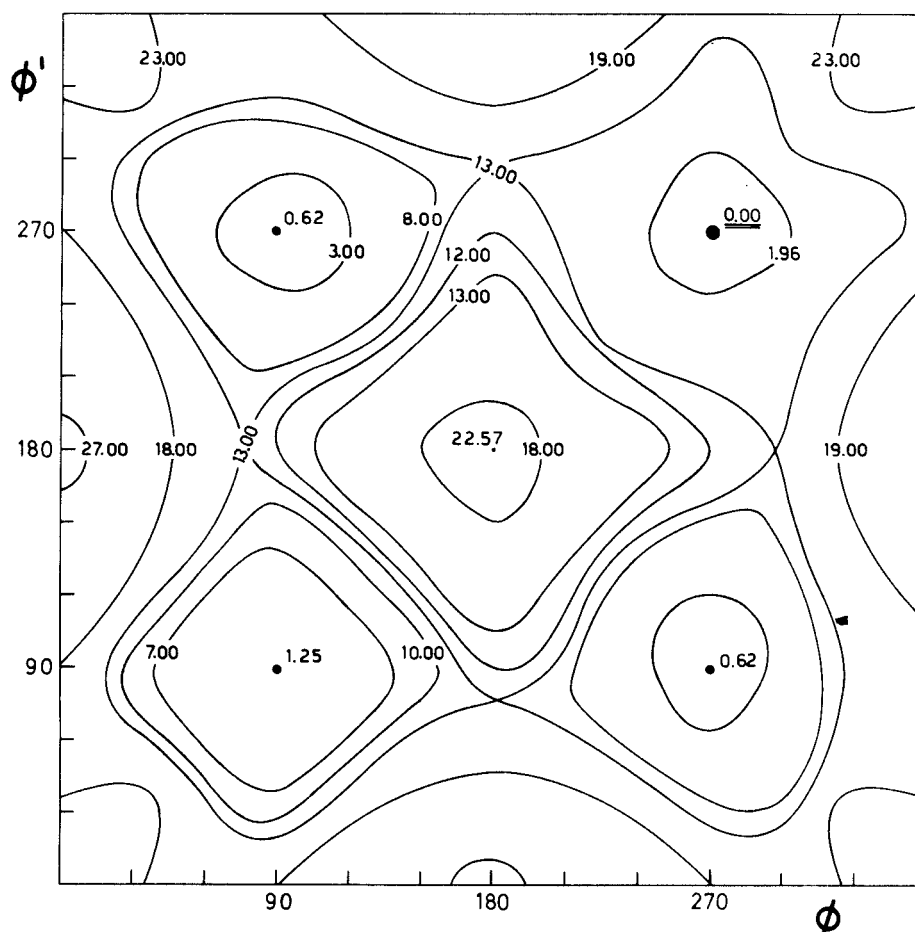

FIGURE II

Map of isoenergy curves for di-2-pyridyl disulfide (CNDO/2 method). The energy scale is relative to an arbitrary energy zero

the bonded carbon atom is achieved upon the C_{py}—S twisting angles corresponding to the favoured conformations. In Table II are reported, as a quantitative evidence, the Hartree–Fock energy matrix elements calculated for the molecule in the minimum energy conformation.

However, the reliability as well as the accuracy of our results will be examined in connection with the experimental information available to date on di-2-pyridyl disulfide. It can be primarily observed that earlier work has shown that the measured dipole moment value of 3.99 D (benzene, 25°) agrees well with that calculated for free rotation about C_{py}—S bonds.[1] Since the concept of free rotation is an artificial one, this would be equivalent to the assumption of approximately equal populations of several molecular conformations differing from one another by the rotation angles of the rotating polar groups. The probability thus arises that the mechanism for the conversion of one conformer of di-2-pyridyl disulfide into the other is as shown schematically below:
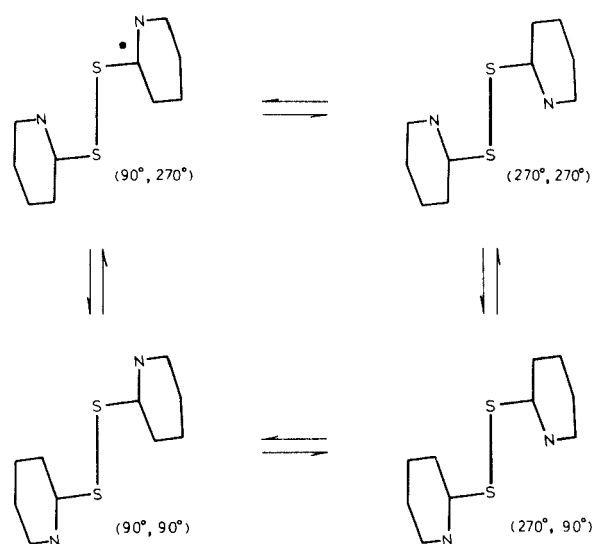

Scheme

TABLE I

Conformational minimum energies and calculated dipole moments for di-2-pyridyl disulfide (CNDO/2 method)

Conformation	Energy (a.u.)	μ (Debye)
(90°, 90°)	−122.390	4.96
(90°, 270°)/(270°, 90°)	−122.391	5.71
(270°, 270°)	−122.392	3.02

In this mechanism, the transition states corresponding to the transition paths: (90°, 90°) ↔ (90°, 270°) ↔ (270°, 270°) ↔ (270°, 90°) ↔ (90°, 90°), are the conformations (90°, 180°), (180°, 270°), (270°, 180°) and (180°, 90°) respectively, which would all have an activation energy of ∼12 Kcal . mol^{-1}, as seen from inspection of the contour map. However, the conversion from one conformation into the other should proceed easily, and for this reason the equilibrium of several forms may be supposed arising by the ready rotation about the C_{py}—S bonds.

The calculated dipole moments and the electronic charges for the energetically most favored conformations of the molecule are presented in Tables I and III, respectively.

The experimentally determined dipole moment in the present case may be considered as an average of the dipole moments of the individual conformers. By making the assumption that the molecule in the gaseous state exists also in the form of a mixture of the four favored "equiprobable" conformers, we obtain a value of $\bar{\mu}_{av}$ = 4.97D*. This assumption is certainly not accurate, since it is clear that these conformations will have different weights in the composition of the

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* This value is obtainable by the relation $\mu^2 = \sum_{i=1}^{n} N_i \mu_i^2$ in which N_i is the relative concentration of the conformer possessing μ_i (see values in Table 1).

TABLE II

Hartree–Fock energy matrix elements of C(1)-S(7) atoms in the minimum energy conformation of di-2-pyridyl disulfide (in a.u.)

| C(1) | S(7) |
	p_x	p_y	p_z	d_{z^2}	d_{zx}	d_{zy}	d_{x2-y2}	d_{xy}
p_x	0.05087	0.17968	0.06297	−0.02532	0.02234	0.07567	−0.11779	0.05755
p_y	0.18147	0.08758	0.06994	−0.02821	0.07589	0.03807	0.09155	0.08727
p_z	0.07406	0.08106	−0.07355	−0.08799	−0.06568	−0.07331	−0.00765	0.07350

TABLE III

Atom charges for di-2-pyridyl disulfide in minimum energy conformations

Atom	$(90°, 90°)$	$(90°, 270°)/(270°, 90°)$	$(270°, 270°)$
C(1)	0.08076	0.08286	0.08281
N(2)	−0.12682	−0.12674	−0.12576
C(3)	0.07807	0.07770	0.07778
C(4)	−0.01194	−0.01194	−0.01268
C(5)	0.03165	0.03245	0.03212
C(6)	0.00208	0.00374	0.00281
S(7)	−0.06823	−0.06390	−0.06358
C(1')	−	0.08050	−
N(2')	−	−0.12872	−
C(3')	−	0.07840	−
C(4')	−	−0.01200	−
C(5')	−	0.03240	−
C(6')	−	0.00270	−
S(7')	−	−0.06740	−
H(3)	0.00132	0.00168	0.00041
H(4)	0.00293	0.00318	0.00243
H(5)	−0.00149	−0.00129	−0.00183
H(6)	0.01167	0.00560	0.00548
H(3')	−	0.00081	−
H(4')	−	0.00218	−
H(5')	−	−0.00262	−
H(6')	−	0.01013	−

mixture of conformers. However, the above considerations indicate that the values of μ, which can be evaluated within the framework of the CNDO/2 theory, reproduce the experimental value of the dipole moment.

The charge distributions obtained by this method (Table III) show that the greatest negative values occur at the N atom positions of the molecule. The other interesting result is the overall electron-withdrawing

effect of the S atoms. It is also evident that for the two unsymmetrical conformers, i.e., $(90°, 270°)$ and $(270°, 90°)$, there is little significant difference in electron density between corresponding atoms in both halves of the molecule.

Pmr Spectra

The spectral parameters for the pyridine ring protons obtained from the computer analysis are given in Table IV,

In the theoretical simulation all the experimental lines were obtained for spectra recorded at a temperature range between 38° and −30°. This means that interconversion of the four predicted conformers in equilibrium is fast, so that the effective *chemical shifts* and coupling constants are averaged. However, the pyridine groups show nonequivalence in the spectra recorded at lower temperatures (from −40° to −60° in MeOH) presumably owing to decrease of the interconversion rates about C_{py}—S bonds. The spectrum at −60° clearly appears as a superposition of distinct patterns corresponding to the individual conformers present. It can be easily deduced that in this spectrum the number of peaks is dramatically increased with respect to the one displayed by the spectra recorded at higher temperatures as a consequence of kinetically restricted rotation of the pyridine rings about C_{py}—S bonds.

Bergson[5] found that p orbital repulsion causes a torsion barrier of 13.8–15.7 Kcal mole^{-1} to internal rotation about the S—S bond in aromatic disulfides. Recent nmr evidence[6] produced a value of 7 kcal mole^{-1} for the barriers in some unsymmetrical acyclic disulfides. Now, although these S—S energetics of rotation are comparable with those calculated in the present work for the C_{py}—S bonds, the −60° spectrum in MeOH can only be explained in terms of conformational changes about these bonds at lower temperatures.

TABLE IV

[1]H-Nmr spectral parameters for di-2-pyridyl disulfide at variable temperature. The mean square deviations (RMS) for the calculated and experimental lines are given

| Temp.	Solvent	Chemical shifts (δ, ppm downfield from TMS)				Coupling constants (Hz)						RMS
		H-3	H-4	H-5	H-6	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}	
38°	MeOH	8.353	7.188	7.676	7.616	4.789	1.652	0.970	7.626	0.726	7.933	0.035
−5°	MeOH	8.379	7.26?	7.751	7.655	4.702	1.685	0.938	7.199	1.278	7.797	0.031
−30°	MeOH	8.414	7.305	7.815	7.673	5.525	1.648	0.875	5.321	1.571	7.699	0.043
38°	CDCl$_3$	8.361	7.053	7.530	7.558	4.421	1.558	0.744	7.640	1.069	7.571	0.040
−30°	CDCl$_3$	8.514	7.224	7.720	7.658	4.735	1.716	0.964	5.844	2.305	7.845	0.042
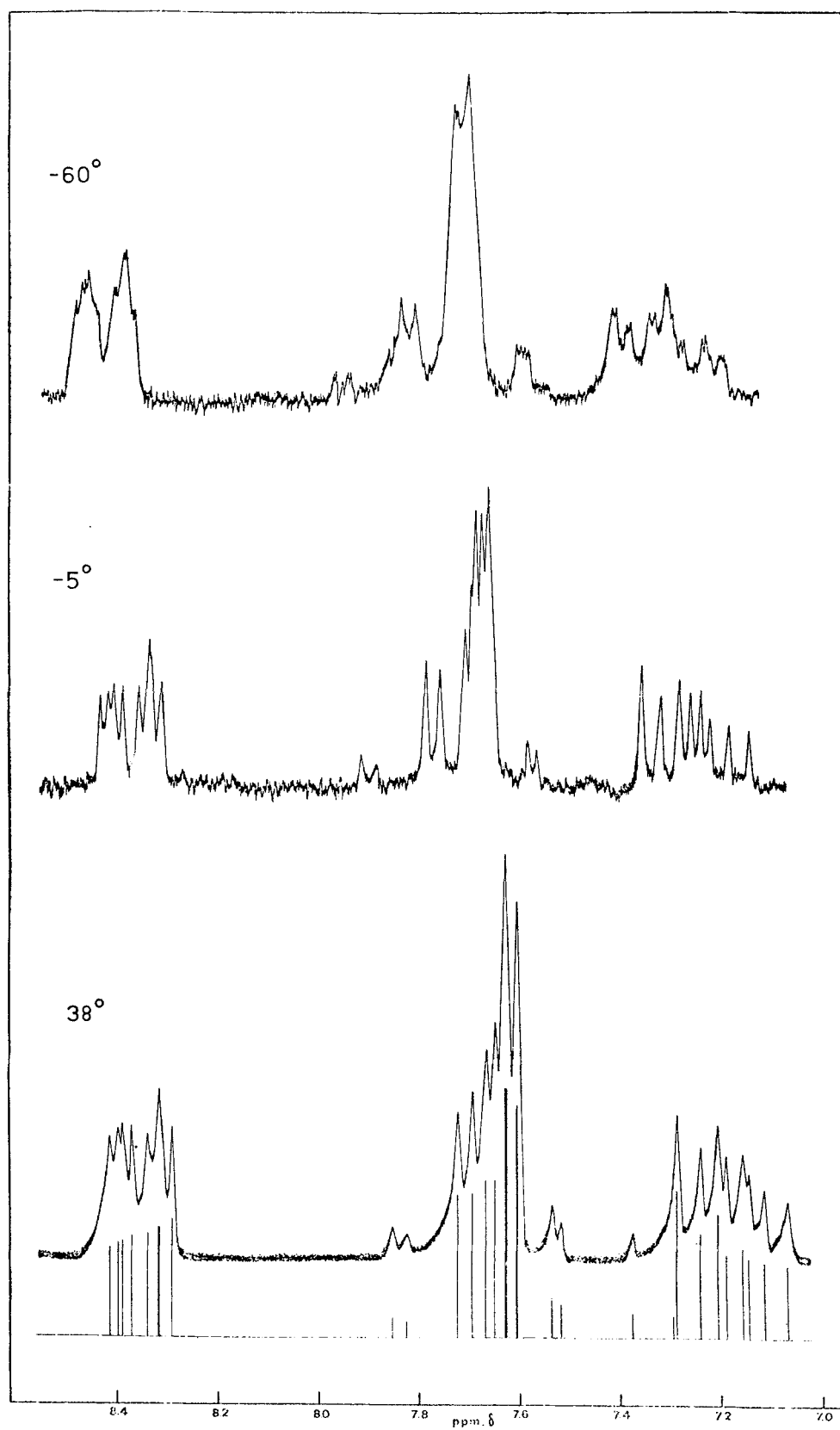
FIGURE III

The 60 MHz proton magnetic resonance spectrum of di-2-pyridyl disulphide in MeOH solution at various temperatures (sweep width 100 Hz). The observed spectrum at 38° is compared to the calculated one.

This view is based on the following considerations: (i) the variation of the S—S dihedral angle in a symmetric disulfide is reasonably expected to affect, by the same extent, the shielding of both pyridine rings; (ii) when we assume C_{py}—S frozen and S—S rotating, magnetic equivalence is to be expected for corresponding protons of the rings in the case of symmetric conformations about C_{py}—S bonds. This condition is not verified at —60°. Moreover, by assuming still S—S rotating and C_{py}—S frozen in unsymmetrical conformation it would be necessary to obtain nonequivalence between the rings at higher as well as at lower temperatures. On the contrary, it can be seen in Figure III that the spectrum at —60° shows significantly more resonance signals than predicted for a four-spin system.

In MeOH solution the signals coalesce at a temperature of about —35°, when interconversion rate about C_{py}—S bonds becomes fast on the nmr time scale. Owing to the difficulty of performing measurements at temperatures below —30° in $CDCl_3$ because of its relatively high freezing point, the spectrum in this solvent cannot be separated into resonances corresponding to different conformations about C_{py}—S bonds. However, it is presumable that results for $CDCl_3$ solution should not differ significantly. In each case the variation of the spectra recorded from 38° to —30° in either of the solvents employed, supplies additional experimental proof of conformational changes which occur about C_{py}—S bonds and thus of the rapid rotation of pyridine groups.

An examination of the spectral parameters reported in Table IV shows that the assignments made for the spectrum at ambient temperature in $CDCl_3$ are in agreement with results of an exact analysis reported for 2-mercaptopyridine in the same solvent.[7] In MeOH as well as in $CDCl_3$ at low temperature, the order of occurrence of the proton resonances in the field has been found to correlate with the calculated charge densities (see Table 3) at the corresponding carbon atoms. In each case, in the compound under examination the ring proton resonances generally occur at lower field than those of 2-mercaptopyridine. Such a deshielding of the pyridinic protons in the disulfide could be essentially caused by the inductive effect due to the S—S group which is enhanced by transmission through the lone-pair electrons on the pyridinic nitrogen.

Experimental

Di-2-pyridyl disulfide (mp 57–8°) was a commercial sample (Aldrich Co.), purified by recrystallizations from alcohol to constant mp and ϵ_{max}.

[1]H-nmr spectra were recorded on a Varian A-60A spectrometer operating at 60 MHz (TMS as internal standard). Room temperature spectra were recorded at a probe temperature of 38°. Low temperature spectra were measured using a Varian V-434/V-6057 accessory, calibrated by means of the standard MeOH and Varian calibration chart. The temperature differences are believed to be accurate to ±0.5°, whereas the absolute accuracy of the temperature measurements is probably somewhat less, owing to the uncertainty in the calibration standard. The samples used for the nmr spectra were either saturated solutions in methanol and $CDCl_3$ at low temperatures, or 5–10 mol% in the same solvents at ambient probe temperature.

Each spectrum was recorded at 50 Hz sweep-width and calibrated by using the usual side-band method. The measured line positions were obtained by averaging the results of four scans forward and backward at a 0.02 Hz s^{-1} scan rate. Average deviations were less than 0.05 Hz.

The iterative LAME[8] computer program was used to analyze the nmr spectra in terms of chemical shifts and coupling constants. The calculated probable errors for the parameters were usually less than 0.06 Hz.

All the computations were carried out using the CDC 6600 computer system at the Computing Centre of the University of Catania.

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