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Ab initio Calculations Including Solvent Effects of the Structure of Pyrazine, 4-Nitropyridine and Dicyanobenzenes Ion Pairs

Pietro Cremaschi, Aldo Gamba and Massimo Simonetta
C.N.R. Centre and Institute of Physical Chemistry, University of Milan

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The potential surfaces of pyrazine, 4-nitropyridine, 1,2-, 1,3-, 1,4- dicyanobenzene radical anions have been calculated within the *ab initio* and electrostatic molecular potential formalism, including the effect of the solvent. These potential surfaces suggest models of ion pairs with alkali cations, which are in agreement with those deduced from related ESR spectra.

Key words: Ion pairs potential surfaces – Solvent effect

1. Introduction

One of the major successes of electron spin resonance spectroscopy has been the detection, through the observation of the hyperfine coupling to the cation, of ion pairs formed by reduction of organic substrates by alkali metals, in solvents of low dielectric constant. The phenomenon of line width variation [1, 2] in the spectrum of such ion pairs has been generally interpreted as an intramolecular migration of the cation between two high electron density regions of the radical anion. The estimation of barrier height between the two sites, the path of the cation migration and the reasons why this migration should occur, have been discussed [2].

There has been a certain amount of speculation on the structure of ion pairs, but little theoretical work has been reported. A review of theoretical methods including different approximations is available in Ref. [3], and in 1974 the results of an *ab initio* MO calculation for the pyrazine$^-$/Li$^+$ ion pair were reported by Hinchliffe and co-workers [4]. More recently we investigated the structure of 4-nitropyridine$^-$/alkali cation ion pairs [5] by calculating the electrostatic potential created by the anion in the surrounding space, following the method proposed by Bonaccorsi, Scrocco and Tomasi [6, 7].

In spite of the importance of the solvent on ion pair formation, only Claxton and McWilliams [8] have tried to take it into account simulating the solvent effect by three molecules of water around Li$^+$, at the apices of a tetrahedron, the other tetrahedron position being the pyrazine anion. This calculation was performed by employing the CNDO/2 method.

The inclusion of the solvent effect should be made easier by the fact that in the case of ion pairs the ESR correlation times indicate that it is an average interaction, rather than a specific one. However there is no generally accepted method by which this average effect can be introduced into the calculation.

We present here a study on the structure of ion pairs in solution, through calculations based on the solvation model, which was suggested by Klopman [9], to take into account the solvent effect. Germer [10, 11] recently reformulated the method to include this effect into the Hartree-Fock SCF-MO formalism, before solving the quantum mechanical problem.

The ion pairs considered here are formed by the alkali cations, and by the radical anions of pyrazine, 4-nitropyridine, 1,2-, 1,3-, 1,4-dicyanobenzenes. Solvents of low dielectric constant such as dimethoxyethane (DME) and tetrahydrofuran (THF), were considered.

2. Methods of Calculation

The *ab initio* UHF [12] wavefunction of the anionic component of the ion pair has been computed by the Gaussian 70 program [13] using a STO-3G basis set [14].

Owing to the lack of experimental geometries for the radical anions, in the case of pyrazine the experimental geometry of the neutral molecule was assumed [15]; planar model geometries were assumed for 4-nitropyridine (see Ref. 16), and for the three isomers of dicyanobenzene radical anion. In the cyano derivatives the benzene ring was assumed as a regular hexagon (r(C–C) = 1.400 Å, r(C–H) = 1.084 Å); for the cyano group the bond distances were taken from experimental values in a related compound [17]: r(C–N) = 1.199 Å, r(C–CN) = 1.370 Å.

The model of Klopman [9] and Germer [10, 11] represents the solvent as a number of induced solvatons, where one solvaton is associated with each atomic centre "s" and carries a charge (Q_s) equal to the opposite of the Mulliken net charge of the associated atomic centre. According to Germer [10, 11] the perturbative terms are:

$$+\frac{\varepsilon-1}{2\varepsilon}\sum_{i=1}^{M}\sum_{s=1}^{N}\frac{Q_s}{r_{si}}\ (M\text{ electrons, }N\text{ nuclei}) \tag{1}$$

which represents the electron/solvaton interaction energy, and

$$-\frac{\varepsilon-1}{2\varepsilon}\sum_{s=1}^{N}\sum_{n=1}^{N}\frac{Q_sZ_n}{r_{sn}} \tag{2}$$

which represents the nucleus/solvaton interaction energy. In Eqs.(1) and (2) ε is the dielectric constant of the solvent.

As we are not dealing with neutral species, we have generalized the evaluation of the solvaton charge by adding the value of q/N to each solvaton; q is the ion charge in a.u.

The solvent interaction matrix elements

$$D_{ij}=\int\psi_i\left[\sum_{s=1}^{N}\frac{Q_s}{r_{s1}}\right]\psi_i\,d\tau(1)$$

have been calculated within the *ab initio* formalism. The new perturbed hamiltonian matrix was diagonalized to obtain the solvent modified total energy and density matrix.

Both the unperturbed and solvent perturbed density matrices were used to obtain the electrostatic interaction energy of the anion radical with a unit positive charge [6, 7]. The reliability of the point charge approximation to describe the behaviour of an alkali cation in the ion pair was discussed in a previous work [5]. We also verified that the annihilation of the quartet spin component in the UHF wavefunctions does not modify significantly the potential surfaces of the considered radical anions.

The calculations were performed on ion pairs in vacuo and in DME ($\varepsilon = 3.49$) and in the THF ($\varepsilon = 7.39$). These solvents have been chosen as they are the most commonly used in ESR ion pair studies.

Potential surfaces were calculated for each anion in the distance range 1.5–3 Å from the radical. These distances have been chosen as they can represent approximate limit values of the regions accessible to the alkali cations in contact ion pairs [4, 5, 25, 26]. In the present model the hard sphere approximation is accepted for the cation and in the given range the distance of minimum approach depends only on the size of the cation.

3. Results and Discussion

3.1. Pyrazine Radical Anion

In Table 1 the net charges calculated for the ion pairs in vacuo, in DME and in THF solvents, together with total energy, are collected. The charge distribution is practically independent of the presence of the considered solvents. This finding implies a quite similar behaviour of the potential in vacuo and in solvents of low dielectric constant, and in this view we report, without any loss of generality, only the potential surfaces of the radical anion in DME. The perspective views of the potential in the molecular plane and in the parallel planes 1.5 and 3 Å above, are shown in Fig. 1.

Assuming that an alkali cation should not approach the anion closer than about 1.5 Å, we have drawn envelope surfaces at distances between 1.5 and 3 Å in the σ_v and σ_h planes of the anion to exactly define the existence and position of each minimum (Fig. 2).

At 1.5 Å four positions of high electron density have been found: two equivalent

Table 1. Net charges and total energies (a.u.) of the pyrazine radical anion

atom	in vacuo	in DME	in THF
N	−0.398	−0.397	−0.396
C	−0.048	−0.047	−0.047
H	−0.003	−0.004	−0.005
E_{tot}	−259.1995	−259.7847	−259.9087

absolute minima are in the molecular plane near the nitrogens, with an energy of −177 kcal/mole in vacuo and −173 kcal/mole in DME and THF. The two equivalent relative minima are found above the molecular plane, but they are more flat, with an energy of −155 kcal/mole in vacuo, −154 kcal/mole in DME and THF, and separated by a barrier of about 6 kcal/mole.

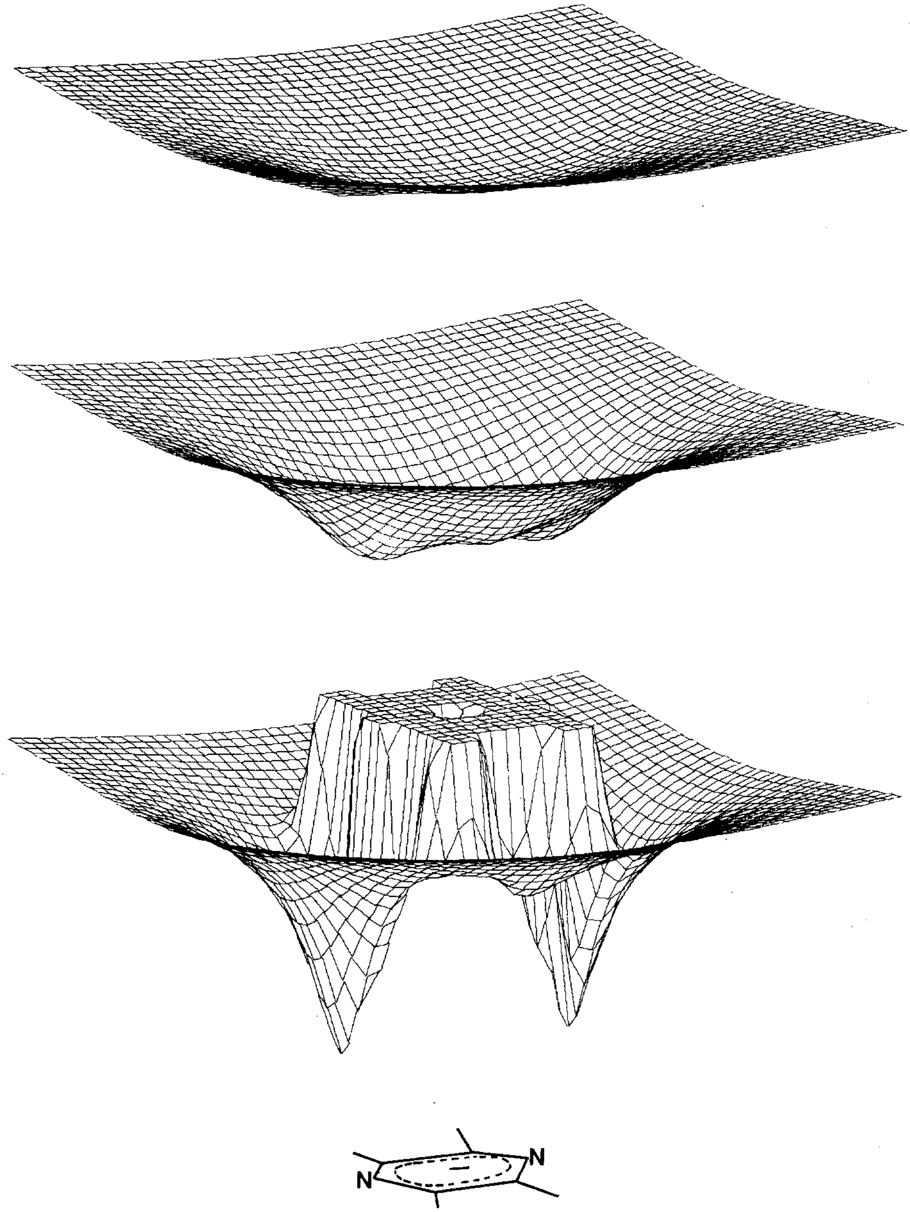

Fig. 1. Perspective views of potential surfaces for pyrazine radical anion in DME; bottom: molecular plane; middle: plane at 1.5 Å; top: plane at 3 Å

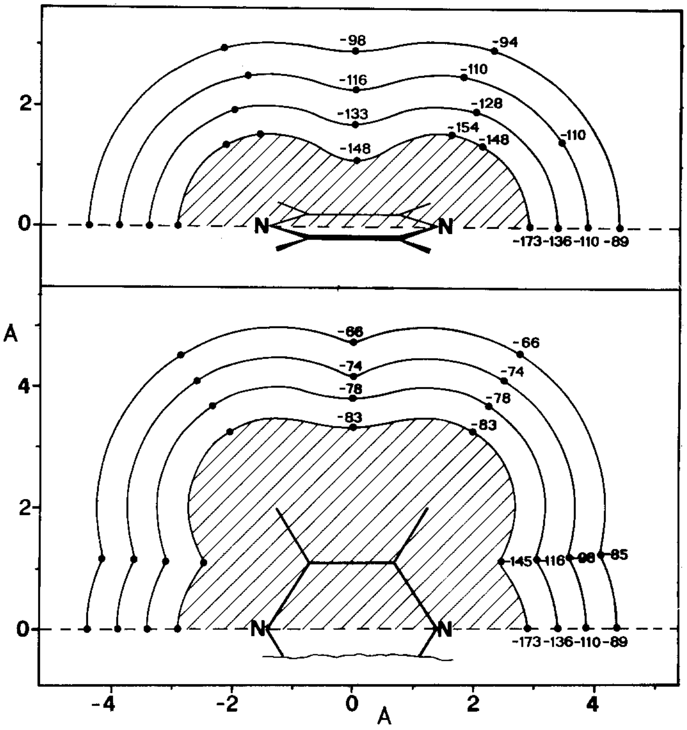

Fig. 2. Equidistance lines (1.5, 2, 2.5 and 3 Å) in the σ_v (upper) and σ_h (lower) plane of the pyrazine radical anion. The most significant values (kcal/mole) of the electrostatic potential on these lines are given

On the other hand envelopes at increasing distances from the anion, show flat potential surfaces with only one minimum in correspondence to the symmetry centre, starting from a distance of 2.5 Å (Fig. 2). See in Fig. 1 the plane at 3 Å, with an energy minimum of −98 kcal/mole in vacuo and in solution.

The alkali ion pairs of pyrazine have been widely studied experimentally by ESR spectroscopy [18–20]. In particular Gooijer and coworkers [20], in a detailed study on the K^+/pyrazine$^-$/DME system, have concluded that the potassium ion is localized above the centre of the pyrazine radical anion, as previously found for Rb and Cs ion pairs [21]. These findings are nicely interpreted by the present calculations, which predict, for large cations, which reasonably cannot approach the anion more than about 3 Å, only one minimum above the centre of the pyrazine anion.

The observation of line width alternation, for defined temperature range, in ESR spectra of Li and Na ion pairs, has been attributed to the intramolecular cation exchange. It implies the presence in the anion of two equivalent sites of minimum energy, separated by small barriers. These regions are well evidenced by the present calculations, both in the molecular plane, and in the plane at 1.5 Å (Fig. 1). The barrier heights are strictly dependent on the distance of the cation from the anion: on going from 1.5 to 2.5 Å from the radical, the barrier

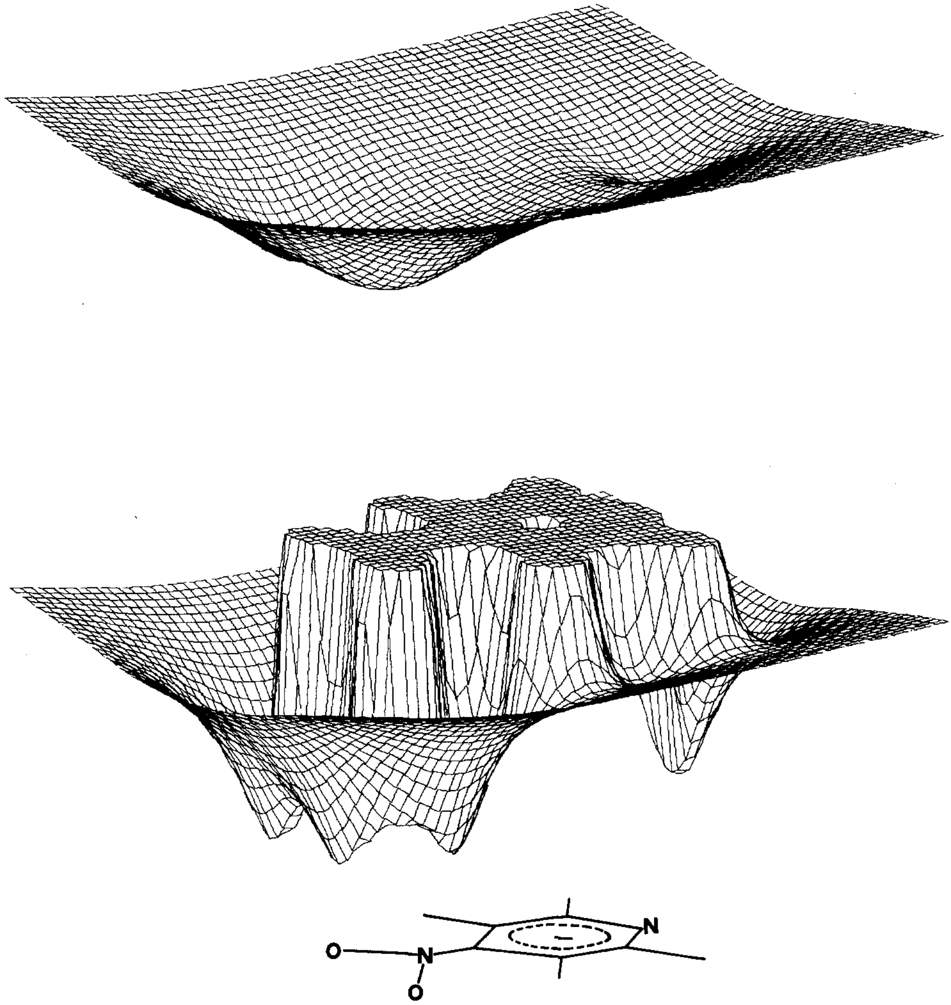

Fig. 3. Perspective views of potential surfaces for the 4-nitropyridine radical anion in DME; bottom: molecular plane; top: plane at 1.5 Å

height sharply decreases from 25 to 6 kcal/mole (Fig. 2). These values can be nicely compared with the estimated value of about 15 kcal/mole for the Li^+ complex in THF and that of 7 kcal/mole for the Na^+ complex in THF reported by Atherton and Goggins [21, 22].

3.2. 4-Nitropyridine Radical Anion

The net charges and the energies in the different media are summarized in Table 2. In this case significant solvent dependent variations of net charges are observed. This trend can be compared with the experimental observations of hfs constants of the free anion of 4-nitropyridine, when small percents of

Table 2. Net Charges and total energies (a.u.) of the nitropyridine radical anion

atom	in vacuo	in DME	in THF
N_1	-0.295	-0.299	-0.300
N_4	$+0.101$	$+0.029$	$+0.013$
O	-0.381	-0.366	-0.362
C_2	0.0	$+0.002$	$+0.003$
C_3	-0.094	-0.083	-0.080
C_4	-0.014	$+0.025$	$+0.033$
H_2	$+0.027$	$+0.023$	$+0.023$
H_3	$+0.051$	$+0.045$	$+0.044$
E_{tot}	-444.2029	-444.6688	-444.7675

water are added to a solution in a low dielectric constant solvent [23]. In fact the strong increase of electron density on the nitro group, that is -0.661, -0.703, -0.711 passing from vacuum to DME and THF, and the smaller variation of electron density on ring nitrogen, that is -0.295, -0.299, -0.300, parallel the trend of hfs constant on the increase of the dielectric constant of the solvent (see Table 5 in Ref. 23).

In spite of these net charge variations on varying the solvent, the potential surfaces evaluated in the different media correspond each other completely.

The perspective view of potential surfaces for DME in the molecular plane and in the parallel plane 1.5 Å above, are shown in Fig. 3.

The anion shows two sites of different high electron density and experimental evidence, inferred from ESR spectra of tight ion pairs formed with Li, Na and K cations in DME [5, 24], is in favour of the localization of the alkali cation in the region of the nitro group. These observations are substantiated by the present calculations. Following the same procedure as for pyrazine, we found two minima in the molecular plane: an absolute minimum at 1.5 Å from the nitro group, with an energy of -133 kcal/mole in DME, and a relative minimum, at 1.5 Å from the ring nitrogen, with an energy of -126 kcal/mole. For distances larger than 2.5 Å, only one minimum is observed in the region of the nitro group. In the distance range 1.5–2.5 Å, where both the absolute and the relative minima are present, the barrier between the two is distance dependent: it goes from 35 kcal/mole at 1.5 Å to 25 kcal/mole at 2.5 Å from the anion. The presence of two non equivalent sites separated by a high barrier, for distances up to 2.5 Å from the anion, and the disappearance of the relative minimum for larger distances, are consistent with the absence of line width alternation in the ESR spectra of ion pairs formed by 4-nitropyridine radical anion with the lighter alkali cations [5].

3.3. *Dicyanobenzene Radical Anion*

The net charge distributions and the energies in vacuo, in DME and in THF for the three isomers of dicyanobenzene radical anions are collected in Table 3. Moderate and regular variations of net charges on account of solvent effects, are found.

Table 3. Net charges and total energies (a.u.) of 1,2-, 1,3-, 1,4- dicyanobenzene radical anions

atom	1,2-dicyanobenzene in vacuo	in DME	in THF	1,3-dicyanobenzene in vacuo	in DME	in THF	1,4-dicyanobenzene in vacuo	in DME	in THF
C(-CN)	+0.020	+0.011	+0.008	+0.027	+0.015	+0.013	+0.015	+0.005	+0.002
N	−0.282	−0.290	−0.291	−0.299	−0.309	−0.310	−0.294	−0.305	−0.307
C_1	−0.080	−0.054	−0.048	−0.106	−0.083	−0.078	−0.093	−0.069	−0.064
C_2				−0.016	−0.006	−0.005	−0.085	−0.080	−0.080
C_3	−0.056	−0.057	−0.057						
C_4	−0.131	−0.128	−0.128	−0.118	−0.113	−0.113			
C_5	−0.069	−0.069	−0.070						
H_2				+0.041	+0.036	+0.034	+0.021	+0.015	+0.014
H_3	+0.026	+0.021	+0.020						
H_4	+0.003	−0.002	−0.004	+0.009	+0.003	+0.002			
H_5				+0.018	+0.012	+0.011			
E_{tot}	−408.8606	−409.3146	−409.4110	−408.8576	−409.2584	−409.3432	−408.8649	−409.2861	−409.3754

In the potential surfaces of the three isomers two equivalent absolute minima are present in the molecular plane at 1.5 Å from the nitrogen atoms of the radical anions. The energies are −130, −127, and −125 kcal/mole (in DME) for ortho, meta and para radicals respectively. A relative minimum is also present in the plane 1.5 Å above the benzene ring with energy of −114, −113 and −112 kcal/mole for the three isomers in DME. The order of magnitude of the barriers between the absolute and the relative minima in the same solvent is about 30 kcal/mole for ortho and meta and 24 kcal/mole for para isomers.

Starting from distances of 2 Å from the anion, only one minimum, over the benzene ring, is present in the case of meta and para isomers, with an energy of −83 kcal/mole at 3 Å. For the ortho isomer two equivalent minima are present in the same range of distances from the radical. They live in the σ_v plane, one in the molecular plane close to the cyano groups, and the other above the benzene ring and they are separated by a barrier of 4–5 kcal/mole in DME. The energy of the minima on the envelope at 3 Å is −85 kcal/mole.

From the analysis of line width variations on temperature of the ESR spectra of ion pairs of ortho and para dicyanobenzene radical anions and lighter alkali cations, intramolecular cation transfer between the equivalent positions of high electron density of the anions, has been ascertained [25]. The potential surfaces calculated in DME at a distance of 1.5 Å from the radical show that in the case of ortho isomer a jump between the two minima along a path in the molecular plane is possible: the barrier is 13 kcal/mole. On the contrary for the para isomer the cation transfer is only possible with a jump out of the molecular plane, with a barrier of about 24 kcal/mole, which sharply decreases to zero on the envelope surface at 2 Å. The path around the radical is energetically unfavoured.

To our knowledge no experimental data for the ion pairs formed by meta dicyanobenzene radical anion and alkali cations are available. The present calculation predicts on the envelope at 1.5 Å a barrier of 35 kcal/mole between the two potential wells: a jump out of the molecular plane is involved. A path lying in the molecular plane requires to overcome an energy barrier of 70 kcal/mole. These results suggest that in the meta isomer the cation transfer would be less favoured, with possible formation of an asymmetric ion pair, at least with lighter alkali cations.

4. Concluding Remarks

The choice of the kind of theoretical approach to be used in the study of the structure and properties of ion pairs is mainly determined by the complexity of the problem and the size of the systems involved.

The present results show that an *ab initio* wavefunction, perturbed by the solvent effect, is accurate enough to calculate the potential surface of ion pairs in solvents of low dielectric constant. In particular the use of an *ab initio* wavefunction improves the results with respect to those obtained by Germer [10] for the charge distribution variations on changing the solvent.

The reliability of the electrostatic molecular potential method in the treatment of ion pair systems [5] has been further confirmed.

Potential surface calculations of this kind allow to interpret and rationalize, in terms of energy barrier heights and cation transfer paths, the structures of the ion pairs and the relative motions of the counter ions desumed from hyperfine pattern and line width variations of their ESR spectra.

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Prof. Dr. M. Simonetta
Istituto di Chimica Fisica
Università di Milano
I-20133 Milano
Italy