STRUCTURE AND REACTIVITY OF CYCLOIMMONIUM YLIDES

Yasser Karzazi and Gheorghe Surpateanu*

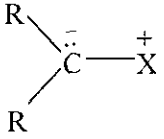
Laboratoire de Synthèse Organique et Environnement, Université du Littoral, Maison de la Recherche en Environnement Industriel de Dunkerque, 145 Route du Pertuis d'Amont, 59140 Dunkerque, France

Abstract - In this review have been presented the early results on the structure of cycloimmonium ylides by X-Ray diffraction patterns as well as UV-Vis, Raman and NMR spectra. The quantum mechanics, *ab initio* and semi-empirical, calculations permited to evaluate all stabilising factors in these specific structures and to demonstrate their reactivity as nucleophilic and 1,3-dipoles reagents in organic synthesis. An important part is affected to the more spectacular synthesis in the class of cycloimmonium ylides involving these molecular systems as intermediates or as compounds with specific properties.

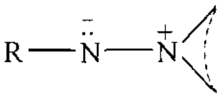
CONTENTS

1. Introduction

Ylides are zwitterionic compounds in which an anion is covalently bonded to a positively charged heteroatom. Ylides can be classified as carbanion ylides (**1**) and as amidines (**2**), R being an an electron withdrawing group.

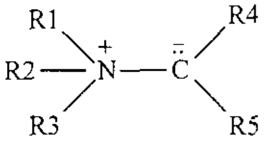


1

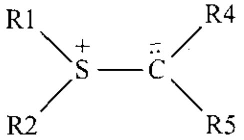


2

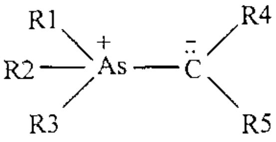
Type (**1**) ylides can themselves be classified by heteroatoms [1] into nitrogen atom ylides (**3**), [2] sulfur ylides (**4**), arsenic ylides (**5**) and phosphorus ylides (**6**).



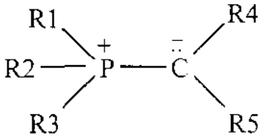
3



4

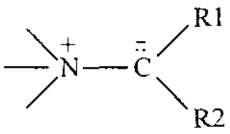


5

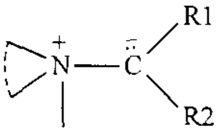


6

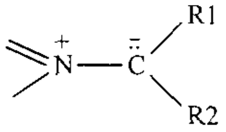
The type (**3**) ylides can be subdivided into the ammonium (**7**), cycloammonium (**8**), immonium (**9**), cycloimmonium (**10**), isonitrile (**11**), and diazonium (**12**) ylides according to the nature of the nitrogen atom.[3]



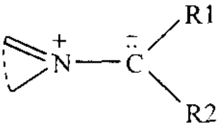
7



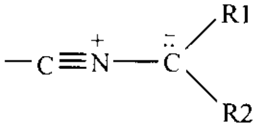
8



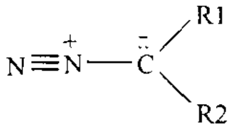
9



10

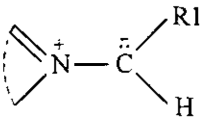


11

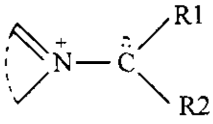


12

In this review we refer only to the cycloimmonium ylides. They can themselves be classified in carbanion monosubstituted (**13**), and carbanion disubstituted (**14**) cycloimmonium ylides by the nature of the carbanion.[4-6] The positive nitrogen atom belongs to an azaheterocycle. The R1 and R2 groups bounded to the ylide cabon atom are strong electron-withdrawing groups : -COPh, -COOR, -CN, $CONH_2$, etc ...



13



14

Generally, the cycloimmonium ylides, as stable compounds, have some interesting properties as analytical reagents [7,8] or semiconducting materials.[9,10] But, their most known applications are as intermediates in various heterocyclic synthesis of new classes of azaheterocyclic compounds [11,12] and ylidic polymers of specific properties. [13]

In this review we develop some aspects on the structure and reactivity of cycloimmonium ylides in connection to our early results.

2. Crystal structures of cycloimmonium ylides

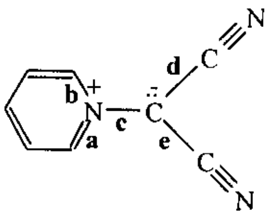
In the literature there are some X-Ray diffraction data on the ylidic compounds.[14,15] Generally for cycloimmonium ylides it is very difficult to establish the spatial distribution of the carbanion with respect to the planar heterocyclic ring.[16-25] For example in the case of dicyanopyridinium methylide [16] the carbanion is almost coplanar to the pyridine ring (Table 1). However, in the case of dinitro-2-methylaminopyridinium methylide [18] the angle between the pyridine ring and the plane described by the ylidic carbon atom and the two neighbouring nitrogen atoms in nitro groups is of 91.75° (Table 1). Theoretically, many others intermediary possibilities between this two extreme situations might be considered. The analysis of the Cambridge Crystallographic Database System 1997 [26] shows that among 160,000 structures of organic and organometallic compounds, only eleven structures correspond to cycloimmonium ylides.[16-25] Thus, it appears very important to increase the number of crystallographic structures resolved by X-Ray diffraction in order to elucidate the spatial distribution between the carbanion and the heterocycle in cycloimmonium ylides. This will be very helpful in order to establish a general harmonic parameterization for the cycloimmonium ylides consistent with the available molecular mechanics models. The structures of the cycloimmonium ylides given in Table 1 have been determined using X-Ray diffraction.[16-25] In this Table, we present some representative results on the bond distances, bond angles and dihedrals. The angle values between the planar aromatic ring (plane P1) and the carbanion plane (P2) is also given in Table 1. Thus, it is possible to differentiate between two structural limits in the case of all measured carbanion disubstituted cycloimmonium ylides :

(i) Near planar carbanion disubstituted cycloimmonium ylides (the first and second ylides in Table 1).

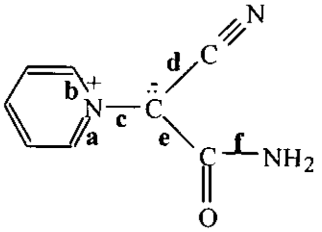
(ii) Nonplanar disubstituted cycloimmonium ylides (other ylides in Table 1).

Table 1 : Experimental X-Ray diffraction data of the cycloimmonium ylides [**i**: Bond distance (Å), **ij**: Bond angle (degree), **ijk**: Dihedral (degree), δ: Angle (P1, P2) (degree)].

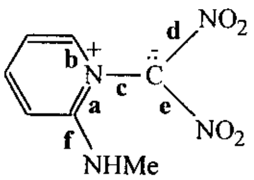
Ylide **(I)**	**a** : 1.37 (1), **b** : 1.37 (1), **c** : 1.42 (1), **d** : 1.41 (1), **e** : 1.41 (1), **ab** : 120.16 (1), **ac** : 119.21 (1), **bc** : 119.21 (1), **ce** : 120.10 (1), **cd** : 120.10 (1), **bcd** : -3.19, **ace** : 3.19, δ : 3
Ylide **(II)**	**a** : 1.356 (5), **b** : 1.355 (4), **c** : 1.422 (4), **d** : 1.401 (5), **e** : 1.434 (4), **ab** : 118.37 (3), **ac** : 121.35 (3), **bc** : 120.27 (3), **ce** : 122.41 (3), **cd** : 117.20 (3), **ef** : 115.92 (3), **bcd** : 8.90, **ace** : 21.74, **cef** : -173.24, δ : 18.17
Ylide **(III)**	**a** : 1.375 (6), **b** : 1.375 (6), **c** : 1.404 (6), **d** : 1.381 (6), **e** : 1.381 (5), **f** : 1.314 (6), **ab** : 122.0 (4), **ac** : 120.1 (4), **bc** : 117.8 (4), **ce** : 117.3 (4), **cd** : 118.6 (4), **af** : 119.0 (4), **bcd** : 92.66, **ace** : -90.53, δ : 91.75
Ylide **(IV)**	**a** : 1.336 (4), **b** : 1.353 (3), **c** : 1.455 (5), **d** : 1.412 (4), **e** : 1.411 (4), **f** : 1.532 (5), **g** : 1.527 (4), **ab** : 120.0 (2), **ac** : 119.5 (2), **bc** : 120.3 (2), **ce** : 119.9 (2), **cd** : 112.6 (2), **ef** : 119.9 (3), **dg** : 120.3 (3), **bcd** : 78.82, **ace** : 89.49, **cef** : -2.22, **cdg** : 176.11, δ : 78.96
Ylide **(V)**	**a** : 1.348 (6), **b** : 1.344 (8), **c** : 1.457 (6), **d** : 1.418 (5), **e** : 1.419 (5), **f** : 1.556 (6), **g** : 1.564 (7), **ab** : 119.9 (4), **ac** : 120.0 (5), **bc** : 119.8 (5), **ce** : 121.7 (3), **cd** : 108.5 (3), **ef** : 121.4 (4), **dg** : 120.7 (4), **bcd** : 97.30, **ace** : 82.28, **cef** : 173.44, **cdg** : -7.74, δ : 97.00
Ylide **(VI)**	**a** : 1.343 (3), **b** : 1.343 (3), **c** : 1.444 (5), **d** : 1.373 (5), **e** : 1.444 (5), **ab** : 120.9, **ac** : 119.4 (2), **bc** : 119.4 (2), **ce** : 115.8 (3), **cd** : 123.4 (3), **bcd** : -92.71, **ace** : -87.29, δ : 90.00
Ylide **(VII)**	**a** : 1.356 (9), **b** : 1.361 (9), **c** : 1.475 (9), **d** : 1.397 (8), **e** : 1.413 (9), **f** : 1.512 (8), **g** : 1.760 (8), **ab** : 120.4 (6), **ac** : 118.5 (5), **bc** : 120.9 (5), **ce** : 116.8 (5), **cd** : 114.4 (6), **ef** : 122.0 (6), **dg** : 115.7 (5), **ace** : -90.0 (7), **dca** : 86.3 (7), **def** : 176.7 (6), **edg** : 2.4 (10), δ : 90.59
Ylide **(VIII)**	**a** : 1.350 (4), **b** : 1.344 (5), **c** : 1.455 (6), **d** : 1.414 (5), **e** : 1.436 (8), **f** : 1.494 (6), **g** : 1.766 (5), **ab** : 119.4 (4), **ac** : 120.8 (3), **bc** : 119.5 (3), **ce** : 117.6 (3), **cd** : 115.3 (4), **ef** : 120.0 (4), **dg** : 116.1 (3), **ace** : -109.8 (5), **dca** : 73.8 (5), **def** : -175.2 (4), **edg** : -2.4 (6), δ : 103.98
Ylide **(IX)**	**a** : 1.336, **b** : 1.382, **c** : 1.441 (1), **d** : 1.443, **e** : 1.393, **f** : 1.496, **g** : 1.416, **ab** : 105.32, **ac** : 128.02, **bc** : 126.57, **ce** : 115.86, **cd** : 114.89, **ef** : 115.66, **dg** : 125.18, **bcd** : -38.24, **ace** : -40.94, **cef** : 166.67, **cdg** : -46.72, δ : 39.47
Ylide **(X)**	**a** : 1.339 (9), **b** : 1.359 (9), **c** : 1.447 (8), **d** : 1.439 (9), **e** : 1.377 (9), **f** : 1.387 (9), **ab** : 120.22, **ac** : 119.13, **bc** : 120.65, **ce** : 121.8 (1), **cd** : 114.1 (1), **ef** : 119.4 (1), **bcd** : -40.4, **ace** : -51.8, **cef** : 171.5, δ : 59.8
Ylide **(XI)**	**a** : 1.350 (7), **b** : 1.357 (7), **c** : 1.448 (7), **d** : 1.434 (8), **e** : 1.391 (8), **f** : 1.369 (6), **ab** : 120.59, **ac** : 120.31, **bc** : 119.10, **ce** : 123.8 (8), **cd** : 113.9 (8), **ef** : 121.3 (8), **bcd** : -50.5, **ace** : -46.0, **cef** : -15.2, δ : 55.5



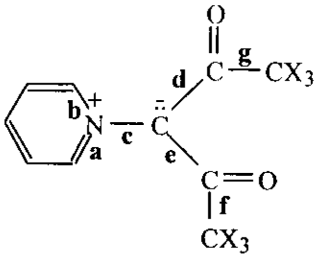
(I) Pyridinium dicyanomethylide



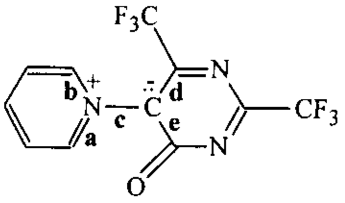
(II) Pyridinium carbamoylcyanomethylide



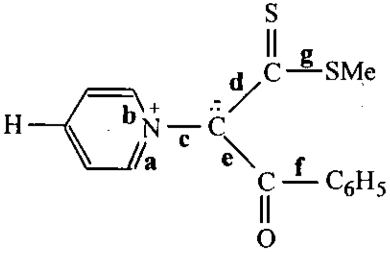
(III) 2-Methylaminopyridinium dinitromethylide



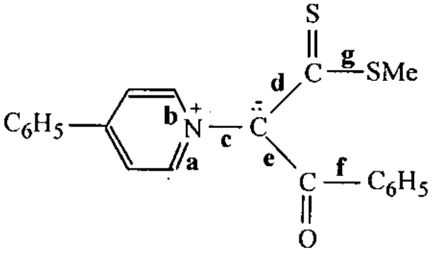
(IV) X = F; Pyridinium di-trifluoroacetylmethylide
(V) X = Cl; Pyridinium di-trichloroacetylmethylide



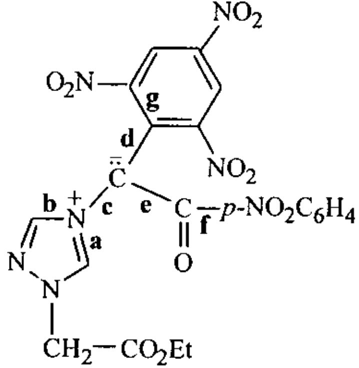
(VI) Pyridinium 4,5-dihydro-4-oxo-2,6-bis(trifluoromethyl)-pyrimidin-5-ylide



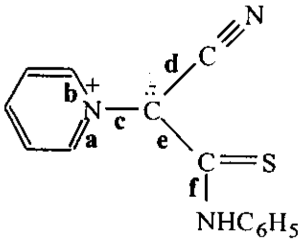
(VII) Pyridinium benzoylmethylthio-thiocarbonylmethylide



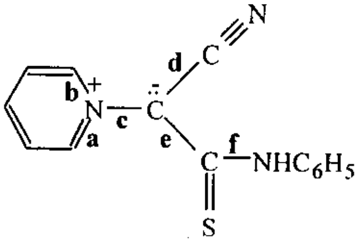
(VIII) Phenylpyridinium benzoylmethylthio-thiocarbonylmethylide



(IX) 1-Ethoxycarbonylmethyl-1,2,4-triazolium 4'-nitrobenzoyl-2",3",4"-trinitrophenylmethylide

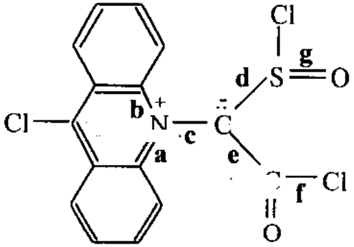


(X) *Z* Isomer

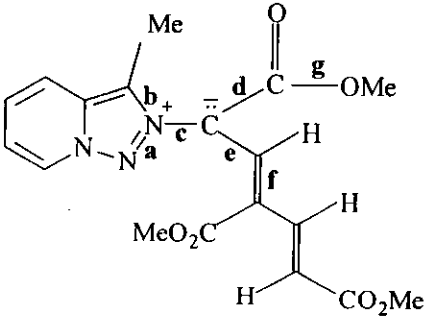


(XI) *E* Isomer

Pyridinium cyano-*N*-phenylthiocarbamoylmethylide



(XII) 9-Chloracridinium chlorocarbonyl-chlorosulfinylmethylide



(XIII) Pyridine 3-methyltriazolium methoxycarbonyl 1-[2,4-dimethoxycarbonyl]butadienylmethylide

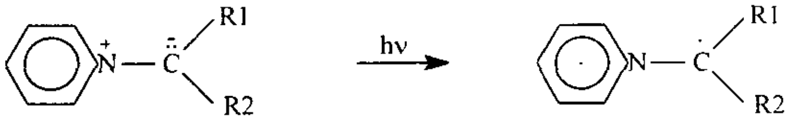
Ylide (**XII**)	**a** : 1.383, **b** : 1.375, **c** : 1.450 (2), **d** : 1.668, **e** : 1.406, **f** : 1.789, **g** : 1.462, **ab** : 122.30, **ac** : 110.81, **bc** : 118.88, **ce** : 116.77, **cd** : 119.81, **ef** : 114.21, **dg** : 107.20, **bcd** : -80.15, **ace** : -75.71, **cef** : 177.06, **cef** : 13.25, δ : 76.89
Ylide (**XIII**)	**a** : 1.341, **b** : 1.350, **c** : 1.440 (2), **d** : 1.414, **e** : 1.380, **f** : 1.399, **g** : 1.345, **ab** : 115.14 , **ac** : 118.13, **bc** : 126.72, **ce** : 121.90, **cd** : 111.98, **ef** : 134.30, **dg** : 114.11, **bcd** : 84.65, **ace** : 88.43, **cef** : -5.81, **cdg** : -175.95, δ : 93.4

Experimentally, only the disubstituted cycloimmonium ylides could be isolated and characterized as stable compounds. The same is not possible in less stable carbanion monosubstituted cycloimmonium ylides. To do it, in order to obtain some structural informations on the carbanion monosubstituted cycloimmonium ylides, a new combined strategy *ab initio* with semi-empirical theoretical calculations has been developed.

Recently,[17,22] the crystal structures of the pyridinium carbamoylcyanomethylide and the pyridine 3-methyltriazolium methoxycarbonyl 1-[2,4-dimethoxycarbonyl]butadienylmethylide have been determined using X-Ray diffraction. The structure of the first compound was found to be nearplanar while the second structure was found to be non planar. These results will be used in the fourth and the fifth parts of this review devoted to a parameterization of the ylidic bond N^+-C^- and thus to propose a transferable force field within the class of cycloimmonium ylides.

3. Cycloimmonium ylides in ultraviolet and visible spectra

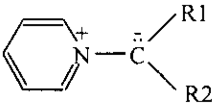
The cycloimmonium ylides present electronic absorption bands both in UV and Vis range. The electronic band from visible of cycloimmonium ylides may be ascribed to an intramolecular charge transfer from the carbanion to the heterocycle n→π*. This assertion has the next reasons:[27,28,31-33] (i) The visible band disappears in acid solutions in which the nonparticipant electrons of the carbanion is blocked by the free protons. (ii) The visible band is less intense in comparison with ultraviolet bands. (iii) The visible band shifts are hypsochromically when passing from nonpolar to polar solvents and from nonprotic to protic solvents.



15 16

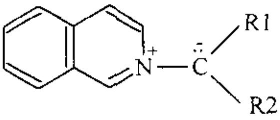
All cycloimmonium ylides have in the UV spectra a bigger number of bands than in visible spectra. It is admitted [27-30] that the UV absorption bands are of π→π* type, on the level of the cation or the carbanion radicals. The deepening of the color of pyridinium ylides accompanying a decrease in the degree of hydration has previously been noted.[34] All ylide systems are strongly chromophore properties which could be explored as analytical indicators or as analytical reagents for the determination of acyl chlorides, anhydrides, isocyanates and isothiocyanates.[5,35] In continuation, the UV bands will be noted by letter U and those from visible with letter V. These letters will be followed by the increasing indices in the order of the frequency rise. The frequency values expressed by wave number measured in these spectra maximum are presented in Tables 2-4.

Table 2 : Electronic absorption data of pyridinium ylides in ethanol.

Number	Compound	ν				
		V	U1	U2	U3	U4
1	R1 = COMe R2 = CO_2Et	26400	35120	42560	49200	-
2	R1 = COMe R2 = COC_6H_5	26560	35040	43540	48640	-
3	R1 = CO_2Et R2 = CO_2Et	24740	40400	48720	-	-
4	R1 = CO_2Et R2 = $CONHC_6H_5$	24090	35920	42960	48800	-
5	R1 = CN R2 = CN	25600	40800	42800	46600	-
6	R1 = COC_6H_5 R2 = COC_6H_5	23500	31680	40040	44000	48460
7	R1 = COC_6H_5 R2 = $CONHC_6H_5$	25500	38800	48600	-	-

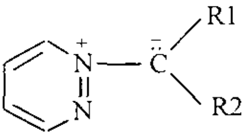
The isoquinolinium ylides present in ethanol solutions a V band of weak intensity which disappears in acid solution and U bands situated in the UV range.[36-38] The V band presents the specific features of a n→π* charge transfer band.

Table 3 : Electronic absorption data of isoquinolinium ylides in ethanol.

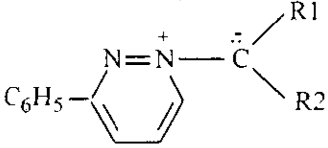
Number	Compound	ν				
		V	U1	U2	U3	U4
1	R1 = COEt R2 = CN	23400	26800	32700	38000	-
2	R1 = CO_2Et R2 = CO_2Et	23500	29700	32200	42000	44000
3	R1 = CO_2Et R2 = CN	23400	27000	32800	37800	44300
4	R1 = CO_2Et R2 = $CONHC_6H_5$	22500	29500	31600	35600	42800
5	R1 = CO_2Et R2 = $CSNHC_6H_5$	22400	32800	43000	-	-
6	R1 = COC_6H_5 R2 = COC_6H_5	24600	31600	43300	-	-

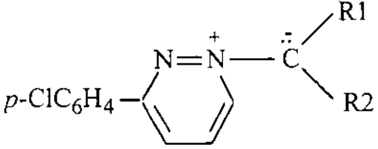
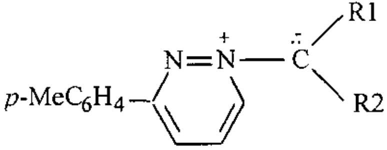
In the Table 4 are given the electronic absorption data of some pyridazinium ylides in ethanol.[38-39]

Table 4 : Electronic absorption data of pyridazinium ylides in ethanol.

Number	Compound	ν				
		V1	V2	U1	U2	U3
1	R1 = H R2 = $COC_6H_4(NO_2)$-*p*	21280	27800	37440	46000	49440
2	R1 = H R2 = $COC_6H_4(OMe)$-*p*	21160	-	37120	44000	49300
3	R1 = $COC_6H_4(NO_2)$-*p* R2 = 2,4,6-$C_6H_2(NO_2)_3$	18000	22000	43000	49250	-

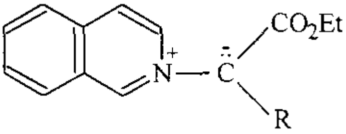
Compound



4	R1 = H R2 = $COC_6H_4(NO_2)$-*p*	21000	26200	38500	-	-
5	R1 = COC_6H_5 R2 = $CONHC_6H_5$	21000	-	33000	38800	45000
6	R1 = COC_6H_5 R2 = $COC_6H_4(NO_2)$-*p*	21600	27500	37400	43000	45500
7	R1 = COC_6H_5 R2 = 2,4,6-$C_6H_2(NO_2)_3$	21900	27800	39200	-	-
	Compound 					
8	R1 = H R2 = $COC_6H_4(OMe)$-*p*	20960	-	36500	44960	49600
9	R1 = 2,4,6-$C_6H_2(NO_2)_3$ R2 = $COC_6H_4(OMe)$-*p*	17440	21440	41200	45180	49000
	Compound 					
10	R1 = H R2 = $COC_6H_4(OMe)$-*p*	20880	-	37440	44500	49120
11	R1 = 2,4,6-$C_6H_2(NO_2)_3$ R2 = $COC_6H_4(OMe)$-*p*	21360	25100	41440	48640	-
12	R1 = H R2 = $COC_6H_4(NO_2)$-*p*	21000	25700	37000	50000	-
13	R1 = COC_6H_5 R2 = $CONHC_6H_5$	21400	-	35400	40500	50000
14	R1 = COC_6H_5 R2 = $COC_6H_4(NO_2)$-*p*	21800	26000	36300	46000	49000
15	R1 = COC_6H_5 R2 = 2,4,6-$C_6H_2(NO_2)_3$	22000	26700	40500	45000	50000

Though the pyridazinium ylides have larger bands, as a result of the molecule complexity degree growth, their electronic absorption spectra are alike those of the pyridinium ylides. Taking into account some of these electronic absorption spectra a new method of calculation of group electronegativity has been pointed out.[7]

The data given in Table 5 have been obtained for a series of isoquinolinium ylides having only R radical variable, by the next equation :



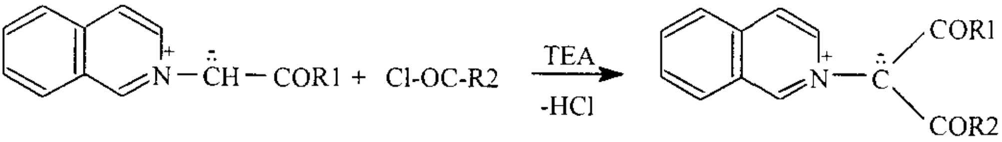
$$\chi_{(ev)} = 0.07E_{max} - 1.3$$

where E_{max} is the energy corresponding to maximum absorption band in visible range.

Table 5 : Group electronegativity

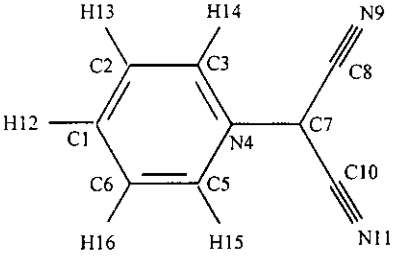
Number	R	E_{max} (kcal/mol)	$\chi_{(ev)}$
1	H	51.5	2.20
2	$-CSNHC_6H_5$	55.2	2.56
3	$-CONHC_6H_5$	58.9	2.82
4	$-CO_2Et$	60.6	2.94
5	-COMe	63.6	3.10
6	$-COC_6H_5$	63.2	3.12
7	-CN	63.5	3.14
8	$-COC_6H_4(NO_2)$-*p*	64.2	3.19

Their specific colors permitted the elaboration of new calorimetric methods of determination of acid chlorides, anhydrides, isocyanates and isothiocyanates.[28]

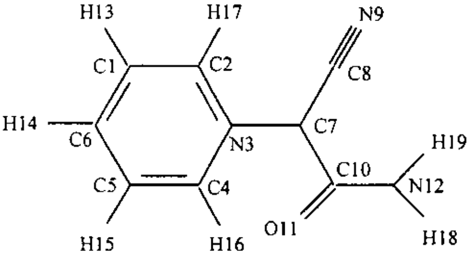


4. Empirical force field for cycloimmonium ylides

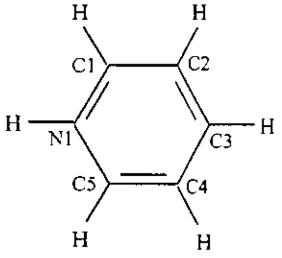
An *ab initio* force field for the pyridinium carbamoylcyanomethylide [40] has been deduced from calculations based on the Density Functional Theory (DFT). The force constants derived from these *ab initio* calculations have been used in order to establish an empirical force field for cycloimmonium ylides, where the transferability of the derived force constants has been tested.[40] In this way, for the first time, a new atom type for the ylidic carbon atom and for the ylidic nitrogen atom has been proposed. The goal of this force field is to provide good quality geometries for cycloimmonium ylide molecules by energy minimization. The predicted structures for pyridinium dicyanomethylide, ylide **(A)** (Scheme 1), pyridinium carbamoylcyanomethylide, ylide **(B)** (Scheme 2), and the pyridinium cation, HPY$^+$ (Scheme 3), using the Tripos force field with parameters established by DFT calculations were in good agreement with those of the experimental X-Ray diffraction data.[16,17,41] A general harmonic parameterization for the cycloimmonium ylides consistent with the available molecular mechanics models has been proposed. In their report, the authors [40] point out the importance of the *ab initio* force field availability to predict the structures of the cycloimmonium ylides.



Scheme 1



Scheme 2



Scheme 3

First, the REDONG program was used [42] in order to carry out vibrational analysis for internal coordinates starting from the DMOL [43] *ab initio* calculation of vibrational frequencies of the ylide **(B)**. Thus, the force constants matrix was transformed into the generalized valence force field. In order to validate this parameterization, the approach consisting of implementing this force field in an empirical potential function was chosen. By using the molecular mechanics method, the determination of the geometry of ylide **(B)** which is similar to X-Ray structure tests the authors parameters.[40] Consequently, the method has been extended to validate transferability of force constants and structure prediction of the ylide **(A)** and the pyridinium cation. A general parameterization for cycloimmonium ylides consistent with the Tripos [44] molecular mechanics force field has been developed. In that study,[40] for the first time, new Tripos atom types for the ylidic carbon atom and the cyclic nitrogen atom have been proposed. This new force field will be very useful for the structure determination of ylidic polymers since it provides good quality geometries for cycloimmonium ylide molecules. Thus, in term of the calculator resources, the very costly DFT calculations on the structure determination of ylidic polymers will be replaced by very cheap molecular mechanics calculations. The following molecular mechanics potential energy function (1) has been used. It corresponds to the empirical method of Tripos,[44] which is implemented in the SYBYL software package. [45] Individual energy terms are given in expressions (2)-(5).

$$E=\sum E_{str}+\sum E_{bend}+\sum E_{oop}+\sum E_{tors}+\sum E_{vdw}+\sum E_{elec} \qquad (1)$$

Bond stretching energy terms: $$V_b=\sum_{i=1}^{N} 1/2K_b(b-b_0)^2 \qquad (2)$$

Angle bending energy terms: $$V_\theta=\sum_{i=1}^{N} 1/2K_\theta(\theta-\theta_0)^2 \qquad (3)$$

Torsional energy terms: $$V_\Phi=\sum_{i=1}^{N} \tfrac{1}{2}V_i^{\omega}\left(1+s_i\cos(|n_i|.\omega_i)\right) \qquad (4)$$

Out of plane bending terms: $$V_\chi=\sum_{i=1}^{N} K_\chi d_i^2 \qquad (5)$$

The bond lengths, bond angles, and torsions are referred to as b_i, θ_i and ω_i, respectively. The subscript "0" indicates equilibrium or reference values, and K_b, K_θ and K_χ are the corresponding force constants. d_i is the distance between the centre atom and the plane of its substituents. Van der Waals parameters were derived from the Tripos force field.[44] In the torsional energy terms, V^{ω}_i refers to torsional barrier in kcal/mol. s_i is equal to 1 (when the elements are staggered) and -1 (when eclipsed). n_i is the periodicity, and ω_i is the torsional angle. The correspondence between atom types and atom names of the structures of the ylide **(A)** and **(B)** and the pyridinium cation are given in Table 6, while the parameters for bond deformation, valence angle deformation, torsion and out of plane bending are given in Tables 7-10, respectively. The values of b_0 and θ_0 are taken from the X-Ray diffraction data of ylide **(B)**.[17] In order to differentiate the new atom types from those of the Tripos force field, the authors added a suffix (y) to the two following new centre types: the first one is the ylidic carbon atom (C2y), the second one is the ylidic aromatic nitrogen atom (Nary). In this way, the ylide carbon atom is taken as a C2 Tripos atom type with a formal charge of -1. In fact the ylide carbon atom is found by means of X-Ray diffraction data [17] to be trigonally hybridized. The ylidic aromatic nitrogen atom is taken as an Nar Tripos atom type with a formal charge of +1. Indeed the ylidic aromatic nitrogen atom is sp^2 hybridized. Note that the values reported for each equivalent bond length, bond angle, torsion and out of plane bending are taken as an average from the corresponding values when available from X-Ray data. When not, in case where the hydrogen atom is involved, the values are taken from the *ab initio* calculation for the ylide **(B)**.[46]

Table 6: Correspondence between atom types and atom names

Atom Type	Atom name for ylide **(A)**	Atom name for ylide **(B)**	Atom name for HPY^+

C2	C10	C10	-
O2	-	O11	-
Nam	-	N12	-
Ham	-	H18, H19	-
C1	C8, C10	C8	-
N1	N9, N11	N9	-
C2y	C7	C7	-
Car	C1, C2, C3, C5, C6	C1, C2, C4, C5, C6	C1, C2, C3, C4, C5
Har	H12, H13, H14, H15, H16	H13, H14, H15, H16, H17	-
Nary	N4	N3	N1

Table 7 : Bond lengths

Atom 1	Atom 2	Bond type	b_0 (Å)	1/2 K_b (kcal/mol.Å)
C2	O2	2	1.240	1498.23
C2	Nam	am	1.349	917.39
C2	C2y	1	1.434	808.215
Nam	Ham	1	1.030	950.81
C1	N1	3	1.138	2310.83
C1	C2y	1	1.401	948.945
C2y	Nary	1	1.422	957.28
Nary	Car	ar	1.355	836.895
Car	Car	ar	1.372	900.37
Car	Har	1	1.097	742.06

Table 8 : Bond angles

Atom 1	Atom 2	Atom 3	θ_0 (deg)	1/2 K_θ (kcal/mol.deg^2)
C2	Nam	Ham	116.40	0.0505
C2	C2y	C1	119.23	0.136
C2	C2y	Nary	122.41	0.234
O2	C2	Nam	120.53	0.1375
O2	C2	C2y	124.67	0.150
Nam	C2	C2y	115.92	0.1455
Ham	Nam	Ham	116.56	0.046
C1	C2y	Nary	117.20	0.148
N1	C1	C2y	178.21	0.048
C2y	Nary	Car	120.81	0.153
Car	Car	Har	121.31	0.051
Nary	Car	Car	121.32	0.0585

Car	Car	Car	119.61	0.053
Har	Car	Nary	113.98	0.0625
Car	Nary	Car	118.37	0.0645

Table 9 : Torsions

Atom 1	Atom 2	Atom 3	Atom 4	Bond type	1/2 V_i^{ω} (kcal/mol)
*	C2	Nam	*	am	27.786
*	C2	C2y	*	1	15.681
*	C1	C2y	*	1	0.142
*	C2y	Nary	*	1	21.743
*	Car	Car	*	ar	21.991
*	Car	Nary	*	ar	21.285

Table 10 : Out of plane bending

Atom	C2	O2	Nam	Ham	C1	C2y	Car	Har	Nary
K_{χ}	14.06	31.07	31.07	7.55	9.91	30.16	17.56	15.90	13.34

The calculations, molecular modeling studies and energy minimizations were performed on a Silicon Graphics (4D/340 VGX) workstation with the SYBYL molecular modelling package (version 6.02).[45] All compounds were built using the sketch option in SYBYL and each structure was optimized using the MAXIMIN2 minimizer (convergence criterion: energy change threshold <0.001 kcal/mol). Energy minimization techniques employed were: (i) steepest descent for the initial minimization and for the relaxing of the starting geometry (maximum 2000 steps), (ii) conjugate gradients technique for the final refined minimization (maximum 2000 steps), (iii) the BFGS was used to reach the minimum energy (maximum 1000 steps).

The experimental and theoretical geometries of the ylide **(B)** are compared in Tables 11, 12 and 13. The structure of this molecule as obtained by the molecular mechanics relaxation (MAXIMIN2 minimizer) is found to be in quite good agreement with respect to the X-Ray geometry and in better agreement with respect to the *ab initio* geometry.

Table 11 : Comparison of the observed and calculated distances in Å for the ylide **(B)**

Atom 1	Atom 2	Distance			
		X-Ray	*ab initio*	Force field [a]	Force field [b]
C2	C1	1.364	1.370	1.375	1.374
C2	N3	1.355	1.369	1.362	1.364

C1	C6	1.375	1.390	1.371	1.370
C6	C5	1.376	1.388	1.372	1.370
C5	C4	1.373	1.375	1.377	1.375
C4	N3	1.356	1.368	1.364	1.366
C8	C7	1.401	1.391	1.403	1.403
C8	N9	1.138	1.178	1.138	1.138
C10	C7	1.434	1.444	1.447	1.450
C10	N12	1.349	1.369	1.349	1.357
C10	O11	1.240	1.248	1.237	1.239
C7	N3	1.422	1.390	1.440	1.443
Standard deviation [c]			0.076	0.007	0.008

a : *Ab initio* charges are in use, b : No charges have been used, c : Standard deviation with respect to X-Ray diffraction data.

Table 12 : Comparison of the observed and calculated bond angle in degrees for the ylide **(B)**

Atom 1	Atom 2	Atom 3	Angle			
			X-Ray	*ab initio*	Force field [a]	Force field [b]
C1	C2	N3	121.21	121.63	122.10	122.18
C2	C1	C6	120.91	120.61	119.54	119.60
C1	C6	C5	117.75	117.20	119.22	119.21
C6	C5	C4	120.17	121.36	119.81	119.92
C5	C4	N3	121.44	120.72	121.69	121.69
C7	C8	N9	178.21	178.55	179.98	179.89
C7	C10	N12	115.92	114.92	121.23	119.72
C7	C10	O11	123.50	124.67	129.50	128.32
N12	C10	O11	120.53	120.39	109.27	111.96
C8	C7	C10	119.23	119.83	118.77	118.73
C8	C7	N3	117.20	116.73	117.30	117.15
C10	C7	N3	122.41	123.36	123.93	124.11
C2	N3	C4	118.37	118.47	117.63	117.41
C2	N3	C7	120.27	119.68	120.42	120.40
C4	N3	C7	121.35	121.85	121.94	122.19
Standard deviation [c]				0.68	3.67	2.86

a : *Ab initio* charges are in use, b : No charges have been used, c : Standard deviation with respect to X-Ray diffraction data.

Table 13 : Comparison of the observed and calculated torsions in degrees for the ylide **(B)**.

Atom 1	Atom 2	Atom 3	Atom 4	Angle

				X-Ray	*ab initio*	Force field [a]	Force field [b]	Search
N12	C10	C7	N3	-173.24	178.71	-180.00	179.99	-158.99
N12	C10	C7	C8	18.31	-4.60	0.00	0.02	21.00
O11	C10	C7	N3	9.41	0.36	0.00	0.02	21.00
O11	C10	C7	C8	-159.04	177.05	180.00	179.99	-159.00
N3	C7	C8	N9	-154.04	126.60	179.53	-179.00	-178.90
C10	C7	C8	N9	15.03	-50.30	-0.47	1.00	1.11
C10	C7	N3	C4	21.74	0.61	0.00	0.01	18.00
C10	C7	N3	C2	-159.77	179.67	180.00	180.02	-161.98
C8	C7	N3	C4	-169.59	-176.17	-180.00	180.02	-162.00
C8	C7	N3	C2	8.90	2.88	0.00	0.01	18.01

a : *Ab initio* charges are in use, b : No charges have been used.

The standard deviations in the case of the ylide **(B)** are 0.007 Å and 0.008 Å for bond lengths with charges and without charges, respectively. The standard deviation between the observed and calculated bond angles, for the ylide **(B)**, is better if no charges are in use (2.86°) than if Mulliken charges computed using *ab initio* technique are in use (3.67°). This deviation can be explained by the following factors: the first one is the fact that the nonbonded distance O1-H5 found using the *ab initio* technique is 1.827Å which suggests a great interaction between these two atoms. Thus the angles X-C10-X, where X is any atom, will be different for calculated and experimental values. The second factor is that the computed force constants correspond to a conformation where the ylide **(B)** adopts a planar geometry, thus the minimized structure by the MAXIMIN2 minimizer must correspond to a planar geometry. Besides, a survey of Tables 14 and 15 shows that the geometry of the ylide **(A)** as obtained by the molecular mechanics relaxation (MAXIMIN2 minimizer) is found to be in good agreement with respect to both experimental and *ab initio* geometries.

Table 14 : Comparison of the observed and calculated distances in Å for the ylide **(A)**.

Atom 1	Atom 2	Distance			
		X-Ray	*ab initio*	Force field [a]	Force field [b]
C10	N11	1.13	1.18	1.14	1.14
C10	C7	1.41	1.39	1.40	1.40
C7	N4	1.42	1.39	1.43	1.43
C7	C8	1.41	1.39	1.40	1.40
C5	C6	1.39	1.37	1.38	1.37
C6	C1	1.39	1.39	1.37	1.37

N4	C5	1.37	1.37	1.36	1.36
N4	C3	1.37	1.37	1.36	1.36
C3	C2	1.39	1.37	1.38	1.38
C2	C1	1.39	1.39	1.37	1.37
C8	N9	1.13	1.18	1.14	1.14
Standard deviation [c]			0.026	0.011	0.011

a : *Ab initio* charges are in use, b : No charges have been used, c : Standard deviation with respect to X-Ray diffraction data.

Table 15 : Comparison of the observed and calculated bond angle in degrees for the ylide **(A)**

Atom 1	Atom 2	Atom 3	Angle			
			X-Ray	*ab initio*	Force field [a]	Force field [b]
C7	C10	N11	180.00	177.22	179.42	179.97
C8	C7	C8	120.10	118.31	118.20	118.33
C8	C7	C10	119.22	123.16	123.60	123.35
N4	C7	C10	120.10	118.52	118.20	118.32
C1	C6	C5	120.29	120.65	119.59	119.66
C8	C5	C6	119.27	121.06	121.61	121.58
C3	N4	C5	120.16	118.94	118.26	118.18
C3	N4	C7	119.21	120.60	120.87	120.91
C5	N4	C7	119.21	120.46	120.87	120.91
C2	C3	N4	119.27	121.01	121.61	121.58
C1	C2	C3	120.29	120.68	119.59	119.67
C2	C1	C6	118.56	117.66	119.34	119.33
N9	C8	C3	180.00	176.39	179.42	179.98
Standard deviation [c]				1.87	1.90	1.80

a : *Ab initio* charges are in use, b : No charges have been used, c : Standard deviation with respect to X-Ray diffraction data.

The standard deviations in the case of the ylide **(A)** are 0.011 Å and 1.803° for bond lengths and bond angles, respectively. It is noteworthy that the results are the same for ylide **(A)** and ylide **(B)** whether or not the atomic charges calculated by *ab initio* technique are used. Indeed, for the ylide 2, note that the root mean square deviation (RMS) with respect to the X-Ray geometry is 0.206 Å and 0.205 Å (with charges and without charges, respectively). The same conclusion is valid for the ylide **(A)** where the RMS with respect to the X-Ray geometry is 0.056 Å and 0.051 Å (with charges and without charges, respectively). The fact that the RMS found for the ylide **(B)** is higher than the corresponding one of the ylide **(A)** can be explained in so far as the force constants derived from the *ab initio* calculations are found to correspond to a planar geometry. Indeed, the angle between the pyridine ring and the plane (C8-C10-N1) in the case of the ylide **(B)** is 4.8° and 18.2° using *ab initio* and X-Ray diffraction, respectively. This is argued if we look to the RMS of ylide **(B)** with respect to the calculated geometry using *ab initio* technique which is 0.071 Å and 0.066 Å (with charges and without charges, respectively). The RMS of the ylide **(A)** with respect to the calculated geometry using *ab initio* technique is 0.052 Å and 0.056 Å (with charges and without charges, respectively). Note that the *ab initio* geometry is in an RMS of 0.088 Å (ylide **(A)**) and 0.199 Å (ylide **(B)**) with respect to the corresponding experimental geometry. Thus the authors [46] concluded that the ylide **(B)** is more constrained in the crystal than the ylide **(A)**. The fact that no more than two crystallographic structures of planar cycloimmonium ylides are available in the literature, where the pyridine ring and the carbanion are coplanar, has limited the extension of the authors *ab initio* force field for other cycloimmonium ylides. However, they have verified their approach for the pyridinium cation; where a good agreement between the calculated and observed data is found. Indeed as shown by the Tables 16 and 17 the standard deviations for bond lengths and bond angles are 0.010 Å and 0.780°, respectively. The RMS with respect to the X-Ray geometry is of 0.030 Å. These results confirm the good adaptability of the proposed parameters to reproduce the structural geometry involving one or more groups contained in the ylide **(B)** structure.

Table 16 : Comparison of the observed and calculated distances in Å for the pyridinim cation.

Atom 1	Atom 2	Distance	
		X-Ray	Force field
C5	C4	1.395	1.375
C4	C3	1.396	1.373
N1	C5	1.396	1.353
N1	C1	1.395	1.353
C1	C2	1.395	1.375
C2	C3	1.395	1.373
Standard deviation with respect to X-Ray diffraction data			0.010

Table 17 : Comparison of the observed and calculated angles in degrees for the pyridinium cation.

Atom 1	Atom 2	Atom 3	Angle	
			X-Ray	Force field
C5	N1	C1	120.01	119.32
C2	C1	N1	120.01	121.09
C3	C2	C1	120.01	119.53
C4	C3	C2	119.99	119.44

C5	C4	C3	120.00	119.53
C4	C5	N1	119.97	121.09
Standard deviation with respect to X-Ray diffraction data				0.78

The parameterization established by the DFT method is able to reproduce or to predict with good accuracy the structures of the cycloimmonium ylides. The comparison of the predicted structures (pyridinium dicyanomethylide, pyridinium carbamoylcyanomethylide and pyridinium cation) with respect to the X-Ray data validates this approach. Thus, it was proposed for the first time a parameterization for the ylidic carbon atom and for the cyclic nitrogen atom involved in the ylidic bond. The implementation in the harmonic potential energy function, Tripos force field, has been successfully applied. It should be emphasized that the present force field has to be used only for structure determination and not for vibrational analysis since in this latter case off diagonal elements with force constant matrix are needed.

5. Spectroscopic force field for cycloimmonium ylides

A Fourier transform Raman spectra of solid pyridinium dicyanomethylide has been reported.[47] Observed frequencies for normal modes have been compared with those calculated from normal coordinate analysis carried on the basis of a DFT force field for pyridinium dicyanomethylide,[47] ylide **(A)**, (Scheme 1). A careful scaling of the internal force constants using correct vibrational assignments is shown to predict quite accurately the experimental vibrational frequencies and the potential energy distribution (PED) for the ylide **(A)**. Thus, a general valence force field for cycloimmonium ylides is constructed on the basis of structure and vibrational spectra of the ylide **(A)**. The DFTcalculations have been performed using the DMol program [43] on a Silicon Graphics 4D/340VGX workstation. The basis set chosen is the DNP (double numeric basis toogether with polarisation function). It is very interesting to note that the geometry optimization has been carried out using the X-Ray structure of the ylide **(A)** [16] without constraining this structure to adopt the C2v symmetry. In order to fit the theoretical to the experimental vibrational frequencies, a direct scaling of the internal force constants has been performed using the Redong program of Allouche and Pourcin.[42] The DFT force constants matrix, expressed in cartesian coordinates, has been transformed to a force constant matrix expressed in internal coordinates. The theoretical frequencies have been obtained by a direct scaling of the force constants when the relative difference between the calculated and experimental frequencies has been minimized using the Redong program. There are 23 scaling factors used for the force constants while scaling the theoretical frequencies. Each of the scaling factors is related to an internal coordinate type (Table 19). Otherwise, only 6 scaling factors among 23 were retained after adjusting the theoretical frequencies with the experimental frequencies (Table 19).

Table 19 : Scaling factors of pyridinium dicyanomethylide.

Internal coordinate	$\nu\mathrm{CN}$	$\nu\mathrm{CC^-}$	$\nu\mathrm{C4C6}$	$\nu\mathrm{CH}$	$\delta\mathrm{NCC^-}$	$\tau\mathrm{CC}$
Scaling factor	0.95	0.92	0.93	0.98	0.90	0.95

Notations for the internal coordinates: ν : stretching, δ :in plane bending and τ : torsion

Using the scaling factors given in Table 19, the potential energy distribution of the ylide **(A)** as function of the internal coordinates and for all of the calculated frequencies by DFT is given in Table 20. A good agreement between the calculated frequencies by DFT and the theoretical frequencies has been obtained. In fact, the root mean square (RMS) found is 4 $\mathrm{cm^{-1}}$. The normal modes assignments of the ylide **(A)** have been discussed, in detail in the literature,[51] on the basis of the assignments of the pyridine [48,49] and the dicyano methane.[50]

Table 20 : Potential energy distribution for the pyridinium dicyanomethylide from DFT calculations.

Exp[a]	Calcd[b]	PED (%)
	73	$\delta\mathrm{C^-CN}(31)+\tau\mathrm{C^-C}(23)+\pi\mathrm{C1}(16)+\tau\mathrm{N^+C^-}(8)+\delta\mathrm{N^+C^-C}(7)+\delta\mathrm{CC^-C}(5)$
124	146	$\delta\mathrm{C^-CN}(50)+\delta\mathrm{CC^-C}(19)+\delta\mathrm{N^+C^-C}(15)$
161	156	$\delta\mathrm{C^-CN}(43)+\delta\mathrm{N^+C^-C}(34)+\delta\mathrm{CN^+C^-}(12)$
	169	$\tau\mathrm{N^+C}(33)+\pi\mathrm{H}(18)+\tau\mathrm{CC}(16)+\delta\mathrm{C^-CN}(13)+\pi\mathrm{C1}(8)+\delta\mathrm{CC^-C}(5)$
272	239	$\tau\mathrm{N^+C}(32)+\pi\mathrm{C1}(30)+\tau\mathrm{CC^-}(12)$
355	346	$\delta\mathrm{CN^+C^-}(42)+\delta\mathrm{C^-CN}(41)$
	402	$\tau\mathrm{CC}(44)+\pi\mathrm{H}(31)+\tau\mathrm{CN^+}(13)+\pi\mathrm{C^-}(5)$
435	430	$\nu\mathrm{N^+C^-}(13)+\pi\mathrm{C^-}(12)+\delta\mathrm{CN^+C}(11)+\delta\mathrm{C^-CN}(8)+\nu\mathrm{C^-C}(7)+\delta\mathrm{CCH}(7)+\delta\mathrm{CCC}(7)+\delta\mathrm{CN^+C^-}(7)+\delta\mathrm{N^+CC}(5)$
	468	$\tau\mathrm{CC^-}(64)+\pi\mathrm{C^-}(11)$
	486	$\tau\mathrm{CC^-}(55)+\pi\mathrm{C^-}(24)+\pi\mathrm{H}(8)$
528	538	$\delta\mathrm{C^-CN}(39)+\delta\mathrm{N^+C^-C}(32)+\nu\mathrm{C^-C}(9)+\nu\mathrm{N^+C}(5)$
	584	$\delta\mathrm{NCC^-}(30)+\nu\mathrm{C^-C}(23)+\delta\mathrm{CC^-C}(18)+\delta\mathrm{N^+C^-C}(13)+\tau\mathrm{CC^-}(8)$
	593	$\tau\mathrm{CC^-}(60)+\pi\mathrm{C1}(20)+\pi\mathrm{H}(6)+\pi\mathrm{C^-}(5)$
	628	$\pi\mathrm{H}(35)+\delta\mathrm{CCC}(16)+\delta\mathrm{N^+CC}(15)+\tau\mathrm{CC}(7)$
646	641	$\pi\mathrm{H}(20)+\delta\mathrm{CCC}(16)+\delta\mathrm{N^+CC}(15)+\delta\mathrm{CCH}(11)+\tau\mathrm{CC}(13)$
697	696	$\delta\mathrm{CCC}(27)+\nu\mathrm{CC^-}(16)+\delta\mathrm{CCH}(14)+\nu\mathrm{N^+C^-}(14)+\nu\mathrm{N^+C}(8)+\delta\mathrm{CN^+C}(5)$
	733	$\pi\mathrm{H}(55)+\pi\mathrm{C^-}(24)+\tau\mathrm{CC}(14)$
	777	$\pi\mathrm{H}(77)+\tau\mathrm{CN^+}(11)+\tau\mathrm{CC}(9)$
	859	$\pi\mathrm{H}(68)+\pi\mathrm{C^-}(14)+\tau\mathrm{CC}(13)$
	888	$\pi\mathrm{H}(69)+\tau\mathrm{CC}(25)$
911	924	$\pi\mathrm{H}(77)+\tau\mathrm{CC}(21)$
993	996	$\nu\mathrm{CC}(31)+\nu\mathrm{N^+C}(26)+\nu\mathrm{C^-C}(21)+\delta\mathrm{CC^-C}(5)$
1017	1012	$\delta\mathrm{CCC}(28)+\delta\mathrm{N^+CC}(19)+\delta\mathrm{CCH}(13)+\delta\mathrm{CN^+C}(8)+\nu\mathrm{N^+C}(8)+\nu\mathrm{C^-C}(6)$
1026	1045	$\nu\mathrm{CC}(40)+\delta\mathrm{CCH}(30)+\nu\mathrm{N^+C}(10)+\delta\mathrm{N^+CH}(8)$
1052	1073	$\delta\mathrm{CCH}(40)+\nu\mathrm{CC}(35)+\delta\mathrm{N^+CH}(8)+\nu\mathrm{N^+C}(7)$
1151	1123	$\delta\mathrm{CCH}(88)+\nu\mathrm{CC}(5)$
1203	1168	$\delta\mathrm{CCH}(57)+\delta\mathrm{N^+CH}(24)+\nu\mathrm{CC}(9)+\nu\mathrm{N^+C}(8)$

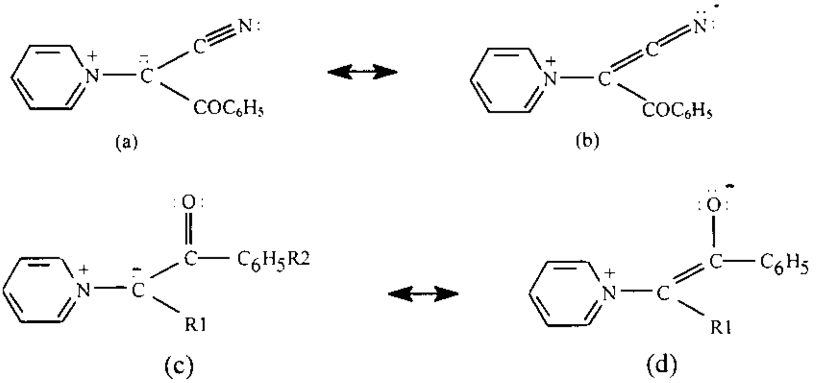
1266	1267	$\nu C^{-}C(50) + \delta N^{+}CH(16) + \delta CCH(12) + \nu N^{+}C(9)$
1287	1304	$\delta CCH(57) + \nu C^{-}C(18) + \delta N^{+}CH(12)$
	1326	$\nu N^{+}C^{-}(61) + \nu C^{-}C(11) + \delta CCH(7)$
	1356	$\nu N^{+}C(41) + \nu CC(36) + \nu C^{-}C(6)$
	1451	$\delta CCH(35) + \nu CC(19) + \delta N^{+}CH(15) + \nu N^{+}C(12) + \nu N^{+}C^{-}(11)$
1482	1469	$\nu CC(44) + \delta CCH(28) + \delta N^{+}CH(11)$
1592	1566	$\nu CC(50) + \nu N^{+}C(19) + \delta CCH(18)$
1617	1622	$\nu CC(56) + \delta CCH(16) + \nu N^{+}C(11) + \delta N^{+}CH(9)$
2152	2156	$\nu CN(81) + \nu C^{-}C(19)$
2179	2177	$\nu CN(86) + \nu C^{-}C(14)$
	3073	$\nu CH(99)$
	3078	$\nu CH(99)$
	3085	$\nu CH(99)$
	3087	$\nu CH(99)$
3094	3093	$\nu CH(99)$

[a] Experimental frequencies (in cm^{-1}), [b] Calculated frequencies (in cm^{-1}) using Redong program

In conclusion, using *ab initio* calculations based on DFT, the PED corresponding to harmonic frequencies of the pyridinium dicyanomethylide has been correctly calculated. Thus, it has been demonstrated that a good force field which can reproduce the experimental frequencies with good precision could be obtained. A careful scaling of the internal force constants using correct vibrational assignments is shown to predict quite accurately the experimental vibrational frequencies and the PED for the pyridinium dicyanomethylide. Thus, the predicted frequencies, obtained after scaling are in a RMS of 4 cm^{-1} with respect to the experimental frequencies. Note that all of the scaled force constants for the ylide **(A)** are given in the literature.[51]

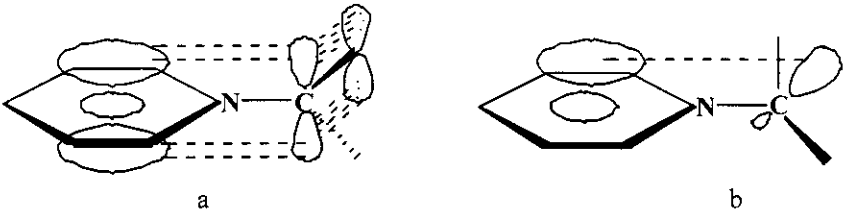
6. Stability of cycloimmonium ylides

The studies on the structures of ylides have formed an active area of chemical research because they are important intermediates in organic synthesis.[1-3] Various aspects of ylide chemistry have been investigated in several comprehensive studies.[52-62] Among the different classes of *N*-ylides, the cycloimmonium ylides have been the subject of numerous and systematic studies [4,5,63,64] because of their higher degree of stability. These studies established that this stability is mainly due to the following three factors : 1. The delocalization of the positive charge on the aromatic ring and the negative charge on the carbanion. 2. The Coulomb attraction between the aromatic positive nitrogen atom and the negative carbanion system. 3. The interaction resonance between the heterocycle and the carbanion. All these factors determine that cycloimmonium ylides exist as chemically stable entities. In all isolable cycloimmonium ylides the negative carbon atom is bonded to electron-withdrawing groups. The total atomic charges calculated by semi-empirical methods were found to be positive for the ylidic nitrogen atoms and negative for the ylidic carbon atoms but greatly under unity.[4,64,65] To our knowledge, no nucleophilic addition on the α carbon atom in the heterocyclic ring has been observed. The theoretical and experimental data show the dominant role of the first factor in the case of stable disubstituted carbanion ylides. Thus, on the one hand, pyridinium cyanophenylcarbonylmethylide and pyridinium cyanoethoxycarbonylmethylide show infrared absorption maximum [66] at 2166 cm^{-1} and 2185 cm^{-1}, respectively (normally ν_{CN} is found to be approximately 2300 cm^{-1}). This shift to low frequencies is attributed to a contribution of the form b in Scheme 4 to the resonance hybrids.[67-69] On the other hand, a shift of the absorption band of the carbonyl function to lower frequencies was observed.[70-74] The $\nu_{C=O}$ absorption band [75-77] for the pyridinium phenacylides is in the range 1490-1500 cm^{-1}, normally $\nu_{C=O}$ is found in the range 1660-1675 cm^{-1}. This indicates, according to some research,[78] an important contribution of the "enol-betaine" form 4d of the resonance hybrid. It is very interesting to note that the second and the third factors enumerated above have only recently been verified,[46,51] respectively. It is well known that the carbanions having two electron-withdrawing groups are more stable.[79]



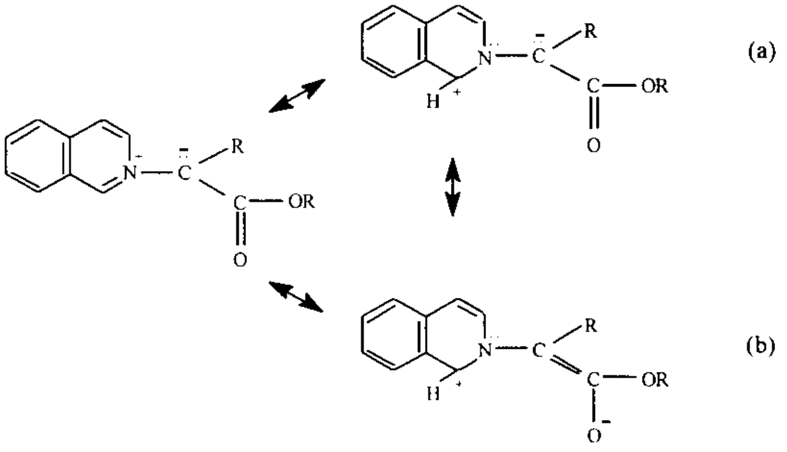
Scheme 4 : Resonance structures for the pyridinium cyanophenylcarbonylmethylide (a) and pyridinium phenacylide (d).

In all the cycloimmonium ylides the ylidic nitrogen atom is sp^2 hybridized while for the ylidic carbon atom sp^2 and sp^3 are the two limits of hybridization. Only in a pair C_{sp^2}-N_{sp^2} configuration could we appreciate an important overlapping between the aromatic ring and the delocalized carbanion cloud (Scheme 5a). Otherwise, in the case of a pair C_{sp^3}-N_{sp^2} configuration, only a small overlapping may occur (Scheme 5b).



Scheme 5 : The two limits of hybridization sp^2 (a) and sp^3 (b) for cycloimmonium ylides.

Previously, the exact knowledge of the spatial structure of pyridinium dicyanomethylide [16] allows some authors to perform semi-empirical (MO) calculations [5,63] using CNDO [80] and EHMO [81] methods. Whatever the structure, the geometries around the ylidic carbon atoms were maintained constant. The geometry of the azaheterocycles and of the ylidic carbon atom radicals were approximated by the data described in the literature.[4,64] Other MO calculations for the monosubstituted carbanion [5,63,82] and disubstituted carbanion [83,84] cycloimmonium ylides have been published. By these calculations the total atomic charges of α ring carbon atoms with respect to the ylide nitrogen atoms are not high. These charges are strongly delocalized on both the heterocycle and carbanion. The largest values of the atomic orbital coefficients of ylide carbon atoms in HOMO frontier molecular orbitals suggest a great reactivity of these atoms as nucleophilic centers.[85] It was concluded for both mono- and disubstituted cycloimmonium ylides that the resonance interaction is not a dominant stabilization factor. The nucleophilic character of ylide carbon atoms in monosubstituted cycloimmonium ylides is larger than that of disubstituted cycloimmonium ylides. However, all cycloimmonium ylides act as 1,3-dipole (Scheme 6a) in the [3+2] and [3+3] cycloaddition reactions [6,86-90] with symmetrical and unsymmetrical dipolarophiles, giving new heterocyclic structures.[53,54] Some cycloimmonium ylides like isoquinolinium or phtalazinium ylides react as 1,5-dipoles (Scheme 6b), in [5+2] cycloadditions.[91]

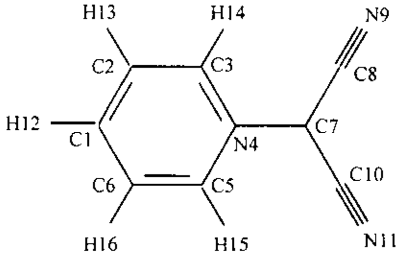


Scheme 6 : The two types of 1,3-dipole (a) and 1, 5-dipole (b) for cycloimmonium ylides.

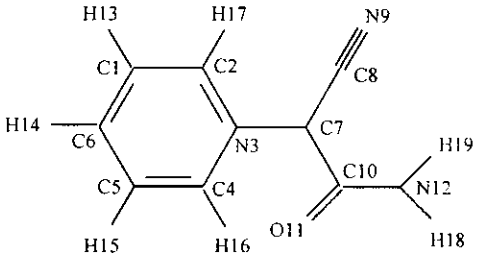
In what follow we are going to present some fundamental electronic and structural features of the planar disubstituted cycloimmonium ylides, nonplanar disubstituted cycloimmonium ylides and monosubstituted cycloimmonium ylides based on semi-empirical calculations and for the first time *ab initio* calculation using the DFT approach.[46,51,52] Note that only the more representative results of these works are presented within this review. The *ab initio* calculations have been performed using the DMol program [43] on a Silicon Graphics 4D/340VGX workstation. The main DMol program calculates variational self-consistent solutions to the density function theory (DFT) equations, expressed in a numerical atomic orbital basis. The atomic basis set chosen for all DMol calculations in this review is the DNP basis set (this notation is used by analogy with Gaussian Double-Zeta (DZ) sets, but the N is used to emphasize the numerical nature of these orbitals), which uses double-numerical basis functions together with polarization functions. The use of various nuclear charges to generate polarization functions is analogous to the variation of zeta in Gaussian basis sets. The DNP basis set is comparable in quality to the Gaussian 6-31G** set. Basis set quality has been analyzed in detail by Delley [92]. The semi-empirical calculations CNDO,[93] INDO,[94] MINDO/3,[95] MNDO,[96] AM1,[97] and PM3 [98,99] have been performed using the Hyperchem[100] or the Mopac programs.[101]

6. 1. Planar disubstituted cycloimmonium ylides

Taking into account the X-Ray diffraction patterns of pyridinium dicyanomethylide, ylide **(A)**, (Scheme 7) and pyridinium carbamoylcyanomethylide, ylide **(B)**, (Scheme 8), respectively, a comparative *ab initio* and semi-empirical studies have been performed.[46]



Scheme 7 : Ylide **(A)**.



Scheme 8 : Ylide **(B)**.

The geometry optimization of ylide **(A)** has been done without symmetry constraints imposed. The C7-C8-N9 unit makes an angle of 3° with respect to the pyridinium ring plane.[16] Otherwise, the C7 atom is

0.003 Å above the pyridinium ring plane.[16] The data obtained from X-Ray diffraction patterns,[16,17] *ab initio* and semi-empirical calculations are reported in Tables 21-25.

Table 21 : Experimental and calculated bond lengths in Å of the ylide **(A)**.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C3-N4	1.37	1.37	1.38	1.40	1.39	1.39	1.37	1.37
N4-C5	1.37	1.37	1.38	1.40	1.39	1.39	1.37	1.37
N4-C7	1.42	1.39	1.38	1.39	1.36	1.38	1.39	1.39
C7-C8	1.41	1.39	1.41	1.41	1.44	1.41	1.40	1.40
C7-C10	1.41	1.39	1.41	1.41	1.44	1.41	1.40	1.40

Table 22 : Experimental and calculated bond lengths in Å of the ylide **(B)**.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C2-N3	1.35	1.37	1.38	1.39	1.37	1.38	1.37	1.36
N3-C4	1.36	1.37	1.38	1.39	1.36	1.38	1.37	1.36
N3-C7	1.42	1.39	1.39	1.42	1.42	1.39	1.40	1.40
C7-C8	1.40	1.39	1.41	1.40	1.43	1.41	1.41	1.41
C7-C10	1.43	1.44	1.47	1.46	1.45	1.46	1.41	1.41
C10-N12	1.35	1.37	1.38	1.42	1.35	1.41	1.38	1.39

The ylide C-N experimental bond length 1.42 Å (1.39 Å using *ab initio*) is not significantly different from what one could expect for a single $C_{sp}{}^{2}$-$N_{sp}{}^{2}$ bond. The values of 1.41 Å (1.39 Å using *ab initio*) in ylide **(A)** and 1.40 Å (1.39 Å using *ab initio*) in ylide **(B)** for the $C_{sp}{}^{1}$-$C_{sp}{}^{2}$ bond are almost the same as the bond length of the single $C_{sp}{}^{1}$-$C_{sp}{}^{2}$ bond in acrylonitrile (1.426 Å),[102] but much smaller than the single C-C bond sp^{1}-sp^{3} in propionitrile (1.458 Å).[103] The other exocyclic bond C7-C10 is 1.43 Å (1.44 Å by *ab initio*) long in ylide **(B)**; this value is smaller than the value of $C_{sp}{}^{2}$-$C_{sp}{}^{2}$ found in the literature (1.46 Å). [104] Thus, it can be concluded for the two ylides that the ylidic carbon atom is almost trigonally hybridized both in the case of ylides (**A** and **B**). The *ab initio* calculations lead to the same conclusion.

Table 23 : Experimental and calculated bond angles in degree of the ylide **(A)**.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C7-N4-C5	119.21	120.46	121.00	121.06	122.53	120.91	121.48	121.40
C7-N4-C3	119.21	120.60	121.00	121.06	122.53	120.92	121.47	121.40
C5-N4-C3	120.16	118.94	118.01	117.88	114.94	118.17	117.05	117.20
C10-C7-C8	119.22	118.31	117.59	117.62	115.97	117.06	124.31	123.86
C10-C7-N4	120.10	123.16	121.20	121.19	122.01	121.47	117.84	118.07

C8-C7-N4	120.10	118.52	121.20	121.19	122.01	121.46	117.85	118.07

Table 24 : Experimental and calculated bond angles in degree of the ylide **(B)**.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C7-C10-N12	115.93	114.92	118.13	118.22	116.66	119.35	121.50	121.44
N3-C7-C8	117.20	116.73	118.86	116.04	113.95	118.87	119.85	119.48
N3-C7-C10	122.62	123.36	122.73	118.72	116.05	122.28	118.61	118.33
C8-C7-C10	119.21	119.83	118.38	125.21	129.90	118.85	127.58	126.31
C7-N3-C4	121.37	121.85	122.60	120.58	121.27	121.01	120.37	120.33
C7-N3-C2	120.26	119.68	119.78	120.09	121.38	120.89	118.83	119.04
C4-N3-C2	118.36	118.47	117.61	119.32	117.35	118.09	125.04	123.93

Table 25 : Experimental and calculated torsions in degree of ylide **(B)**.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C4-N3-C7-C10	21.74	-0.61	16.62	53.09	69.42	-1.39	-0.14	0.13
C2-N3-C7-C8	8.90	-2.88	13.51	50.88	65.77	-0.61	-0.37	-1.09
N3-C7-C10-N12	-173.24	178.71	-175.70	-165.06	-177.88	-172.10	-177.47	-175.43

The small difference between the calculated bond angle C7-C8-N9 (176.39°) and C7-C10-N11 (177.22°) for ylide **(A)** and C7-C8-N9 (178.55°) for ylide **(B)** and reference is frequently found in the literature.[105-109] A previous *ab initio* calculation [110] for the $C(CN)_2$ molecule lead to a value of 177°. In ylide **(A)**, the pyridinium ring is coplanar with the carbanion and the two cyano groups making an angle of 3.7° (3° by X-Ray and 0° by all the semi-empirical methods) with respect to the pyridine ring plane (Table 26). In the case of the ylide **(B)** the two substituents are inclined in same plane at an angle of 18.2° and of 4.8° by DFT (Table 26).

Table 26 : Angles between P1 and P2 planes.

	X-Ray	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
ylide **(A)**	3°	3.7°	0°	0°	0°	0°	0°	0°
ylide **(B)**	18.2°	4.8°	15°	51.9°	67.5°	1.1°	1.2°	0.4°

P1 is the plane described by the pyridine ring.
P2 is the plane described by the carbanion and it's binded carbon atoms.

The calculated geometry of ylide **(A)** using *ab initio* technique is found in a root mean square deviation (RMS) of 0.088 Å (Table 27) with respect to the X-Ray structure. The AM1 and PM3 semi-empirical methods give the best RMS for the calculated geometry with respect to X-Ray diffraction data (0.039 Å and 0.040 Å, respectively). Otherwise, the calculated geometry of ylide **(B)** using *ab initio* technique is in an RMS of 0.199 Å with respect to X-Ray diffraction geometry. The geometries computed by the AM1 method compare most favorably with the experimental one (0.089 Å), this method also reproduces the angle between the planes P1 and P2 (15° by AM1 and 18.2° by X-Ray diffraction data). In the case of ylides (**A** and **B**), cycloimmonium ylides, the AM1 method is thus the appropriate semi-empirical procedure as it gives the closest agreement with the experimental X-Ray diffraction results.

Table 27 : Calculated RMS with respect to X-Ray geometry (Å).

	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
ylide (**A**)	0.088	0.039	0.049	0.072	0.040	0.062	0.066
ylide (**B**)	0.199	0.089	0.384	1.174	0.195	0.205	0.198

The *ab initio* charges given in Tables 28 and 29 obtained by Mulliken populations show that:

- There is a good agreement between the charges of ylides (**A** and **B**) on the level of their common atoms.

- The ylide nitrogen atoms have small positive charges, 0.118 and 0.121 for ylides (**A** and **B**), respectively. This shows that the positive charge is not localized on the nitrogen atom but rather is delocalized on all the atoms of the pyridine ring.

- The ylide carbon atoms are insignificantly charged, 0.063 in ylide (**A**) and 0.057 in ylide (**B**). This demonstrates that the formal negative charge often accepted for the ylidic carbanion atom is delocalized.

- The total atomic charges of cyclic carbon atoms adjacent to the ylide nitrogen atom have negative charges (-0.125 for ylide (**A**) and -0.121, -0.125 for ylide (**B**)). This precludes any nucleophlic addition on the α carbon atom in heterocyclic ring and is in good agreement with the fact that no nucleophilic addition on such atoms has been observed.

- The nitrogen atom of the nitrile group is negatively charged -0.227 and -0.275 in ylides (**A** and **B**), respectively.

- The oxygen atom in the amide group has a negative charge of -0.469. The nitrogen atom, in the amide group, has a strong negative charge which suggests a strong delocalization of the negative charge on the ylidic carbon atom towards the oxygen atom in the amide groups. This is proven by the fact that ylide (**B**) acts as 1,5-dipole in cycloaddition reactions.

Table 28 : Effective atomic charges from Mulliken populations of ylide (**A**).

	DFT	Scaled charges*	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C3	-0.125	-0.143	-0.140	-0.032	-0.133	-0.398	0.035	0.025
N4	0.118	-0.135	0.189	0.091	0.400	0.868	0.203	0.178
C5	-0.125	-0.143	-0.140	-0.032	-0.133	-0.398	0.035	0.025

C7	0.063	0.072	-0.206	-0.138	-0.273	-0.361	-0.141	-0.136

• : The scaling of *ab initio* charges was done in the Sybyl software package,[45] taking into account the experimental dipole moment of the ylide (**A**).

Table 29 : Effective atomic charges from Mulliken populations of ylide (**B**).

	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
C2	-0.121	-0.128	0.065	0.010	-0.387	0.060	0.048
N3	0.121	0.190	0.055	0.370	0.876	0.202	0.169
C4	-0.125	-0.104	0.094	0.025	-0.408	0.001	0.011
C7	0.057	-0.333	-0.347	-0.507	-0.543	-0.216	-0.187

A survey of data in Tables 28 and 29 shows that the MINDO/3 and PM3 semi-empirical methods give values which are inconsistent with those obtained at the *ab initio* level. The ylidic nitrogen atomic charges obtained are 0.400, 0.878 in ylide (**A**), and 0.370, 0.876 in ylide (**B**) by MINDO/3 and PM3, respectively. The atomic charges computed by the MNDO and AM1 methods are much closer to those computed by *ab initio* methods using CNDO and INDO. The result of using the Sybyl software package [45] to scale the *ab initio* charges of ylide (**A**) in order to reproduce the experimental dipole moment is presented in Table 28. As the calculated dipole moment by *ab initio* technique is almost the same as the experimental one the scaled charges are in good agreement with those calculated using *ab initio*. In this way, the authors [46] have demonstrated the existence of the resonance interaction factor between the carbanion and the pyridine ring as one of the three stabilization factors of the cycloimmonium ylides. Therefore the classical representation of these systems with formal charges localized on the nitrogen and on the carbon of the ylide bond is far from the reality. Table 30 shows a comparison between the experimental and calculated dipole moments for the ylides (**A** and **B**), although the dipole moments are notoriously difficult to calculate and require extensive basis sets at the *ab initio* level.

Table 30 : Experimental and calculated dipole moments (Debye).

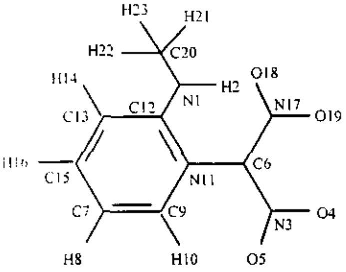
	Exp.	DFT	AM1	MNDO	MINDO/3	PM3	INDO	CNDO
ylide (**A**)	9.2[a]	7.9	7.5	7.3	5.3	7.5	7.8	8.1
ylide (**B**)	-	4.1	4.3	6.4	5.3	4.3	4.8	6.2

a : In dioxane.[111]

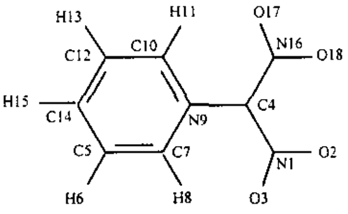
The MINDO/3 method fails another time to reproduce observable experimental data, while all other methods are reasonably close to the value calculated by the *ab initio* method. As the MINDO/3 was based on the INDO approximation, which could not represent lone pair - lone pair interactions; MINDO/3 had difficulty with systems containing lone pairs. To rectify this, a new method, MNDO, was published by Dewar and Thiel.[97] However, in order to overcome the inability of MNDO to reproduce the hydrogen bond in water dimmer, the AM1 method has been published [98] as a second parametrization of MNDO. PM3 is a third.[99,100] Among the six semi-empirical methods presented in this study, the AM1 method has the merit to reproduce at the same time the experimental observables and *ab initio* results for ylides (**A** and **B**) with a high degree of accuracy.

6. 2. Nonplanar disubstituted cycloimmonium ylides

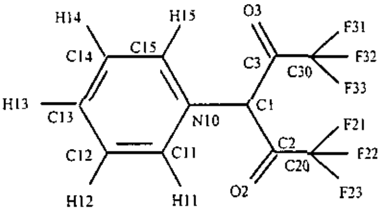
Taking into account the X-Ray diffraction patterns of 2-methylaminopyridinium dinitromethylide (ylide **C**) (Scheme 9), pyridinium dinitromethylide (ylide **D**) (Scheme 10), and pyridinium di-trifluoroacetylmethylide (ylide **E**) (Scheme 11), respectively, a comparative *ab initio* and semi-empirical studies have been performed.[51,52]



Scheme 9 : Ylide (**C**).



Scheme10 : Ylide (**D**).



Scheme 11 : Ylide (**E**).

The properties of ylidic systems presented above have been measured by X-Ray diffraction except for the ylide (**D**), where the experimental data is not available but must be very close to the one of the ylide (**C**). The optimization geometries of the ylides (**C**, **D** and **E**) have been performed using the DFT approach. The data obtained from X-Ray diffraction patterns and DFT calculations, for the ylides (**C**, **D** and **E**) are given in Tables 31-36.

Table 31 : Experimental and calculated data bond lengths (Å) for the ylide (**C**).

Atom 1	Atom 2	X-Ray	DFT
N1	C12	1.314	1.332
C6	N3	1.381	1.407
C6	N11	1.405	1.407
C6	N17	1.381	1.373
N11	C9	1.374	1.366
C12	N11	1.375	1.381

Table 32 : Experimental and calculated data bond angles (degrees) for the ylide (**C**).

Atom 1	Atom 2	Atom 3	X-Ray	DFT
N17	C6	N11	118.57	121.37
N11	C6	N3	117.30	115.90
C6	N11	C12	120.07	122.16
C6	N11	C9	117.80	116.47

C12	N11	C9	122.02	120.38
N1	C12	N11	118.95	116.80

Table 33 : Experimental and calculated data bond lengths (Å) for the ylide (**D**).

Atom 1	Atom 2	X-Ray	DFT
C4	N1	1.381	1.397
C4	N9	1.405	1.403
C4	N16	1.381	1.396
N9	C7	1.342	1.355
N9	C10	1.375	1.356

Table 34 : Experimental and calculated data bond angles (degrees) for the ylide (**D**).

Atom 1	Atom 2	Atom 3	X-Ray	DFT
N16	C4	N9	118.57	117.63
N9	C4	N1	117.30	117.08
C4	N9	C10	120.07	120.29
C4	N9	C7	117.80	119.50
C10	N9	C7	122.02	120.21

Table 35 : Experimental and calculated data bond lengths (Å) for the ylide (**E**)

Atom 1	Atom 2	X-Ray	DFT
C1	C2	1.418	1.411
C1	C3	1.450	1.412
C1	N10	1.461	1.456
C2	C20	1.523	1.532
C3	C30	1.539	1.527
N10	C11	1.339	1.336
N10	C15	1.341	1.353

Table 36 : Experimental and calculated data bond angles (degrees) for the ylide (**E**).

Atom 1	Atom 2	Atom 3	X-Ray	DFT
C2	C1	N10	119.50	119.90
C3	C1	N10	111.70	112.60
C1	C2	C20	119.10	119.90
C1	C3	C30	120.90	120.30
C1	N10	C11	120.60	120.30
C1	N10	C15	119.30	119.50
C11	N10	C15	119.80	120.00

The standard deviations between the calculated and experimental values, for bond lengths and bond angles, are (0.005 Å, 0.17°), (0.006 Å, 0.12°) and (0.005 Å, 0.02°) for the ylides (**C**, **D** and **E**), respectively. The X-Ray diffraction data, for the ylides (**C** and **E**), and the DFT calculations for the ylides (**C**, **D** and **E**) show that the ylidic carbon atom and the nitrogen atom in the heterocyclic ring are trigonally hybridized (the sum of the angles around each one of these atoms is 360°). Thus, the experimental and calculated geometries, using the DFT approach, are in good agreement. In addition, the calculated bond lengths and bond angles of the pyridinium ring using the DFT approach for the ylides

(**C**, **D** and **E**) are in good agreement with those corresponding for the ylides (**A** and **B**).[46] The experimental N-O bond lengths of the ylide **(C)** [18] are longer than those of nitrobenzene,[112] and closely resemble those reported for 2,4,6-trinitrophenetole,[113] where the nitro groups are involved in negative charge delocalization. It is very important to note that for the ylide **(C)**, the *exo*-[N3-O4 (1.234 Å, 1.235 Å by X-Ray diffraction and DFT, respectively) and N17-O19 (1.235 Å, 1.230 Å by X-Ray diffraction and DFT, respectively)] nitro bond lengths are longer than the *endo*-[N3-O5 (1.253 Å, 1.257 Å by X-Ray diffraction and DFT, respectively) and N17-O18 (1.250 Å, 1.260 Å by X-Ray diffraction and DFT, respectively)] nitro bond lengths (Table 31). The DFT calculations lead to the same discrimination between the *endo* and *exo* N-O bond lengths in the case of the ylide **(D)** (Table 33). These results may reflect a greater concentration of negative charge of the *endo*-oxygen atoms, which are closer to the positively charged ring. This idea will be verified below with charge calculations using the DFT approach. The shortness of the ylidic bond, in the case of the ylide **(C)**, [1.404 Å (1.407 Å using DFT) rather 1.42 Å for the ylides (**A** and **B**)] appears to be a function of charge attraction rather than conjugation. This result will be connected to the nature of the charges calculated for ylidic carbon atom and the α carbon atoms in the heterocyclic ring, using DFT (see below), in order to demonstrate for the first time the existence and importance of the Coulomb attractive strength, between the heterocyclic aromatic ring and the carbanion, as one of the principal factors in the stability of cycloimmonium ylides.

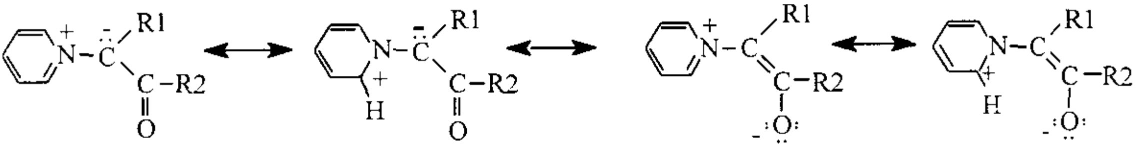
A survey of the total atomic charges shows that the aromatic nitrogen atoms are positively charged 0.118, 0.121, 0.108 and 0.075 for the ylides (**A**, **B**, **D** and **E**), respectively. However, for the ylide **(C)**, the aromatic nitrogen atom reveals moderate negative charge -0.018 (probably due to an additional delocalization given by the NHMe group). Thus, the positive charge of the ylide nitrogen atom is delocalized on the pyridine ring. This suggest, for the ylides (**A**, **B**, **C**, **D** and **E**) no reactivity on the level of the aromatic nitrogen atoms. In fact, experimentally the aromatic nitrogen atom does not interact in chemical reactions, except when the ylidic bond is broken in order to give the heterocycle and the corresponding carbene.[75,114] The negative charges found for the cyclic carbon atoms adjacent to the ylide nitrogen atom are: -0.125, -0.121, -0.124, -0.132 and -0.149 for the ylides (**A**, **B**, **C**, **D** and **E**), respectively. These negative charges preclude any nucleophlic addition on the α carbon atom in the heterocyclic ring. This is in good agreement with the experiments, where no nucleophilic addition on such atoms has been observed. Otherwise, the nucleophility of the ylidic carbon atom is bigger for monosubstituted cycloimmonium ylides than for the disubstituted ones which agrees with the finding that the reactions are dependent on the substituents.[63,83,84] Noteworthy, the disubstituted cycloimmonium ylides appear as chemical stable entities and are thus resolved by X-Ray diffraction.

Thus, it is normal to find insignificant charges for the ylidic carbon atoms because the formal negative charge often accepted for the ylidic carbanion is delocalized.[46] Indeed, for the ylides (**A** and **B**), where the interaction resonance factor has been proved, we find a small positive charge: 0.063 and 0.057, respectively. In the case of ylides (**C**, **D** and **E**), such interaction resonance factor is precluded because of the non planarity of these systems. However, the ylidic carbon atoms have small negative charges -0.022, -0.040 and -0.009 for the ylides (**C**, **D** and **E**), respectively.

It is very interesting to remark that the total atomic charges corresponding to the ylides (**A** and **B**) (planar disubstituted cycloimmonium ylides) and those of the ylides (**D** and **E**) (nonplanar disubstituted cycloimmonium ylides) are comparable on the level of the ylidic carbon atoms, the aromatic nitrogen atoms and the α carbon atoms in the heterocyclic ring. The resonance interaction cannot explain these comparable results because the carbanion and the pyridinium ring are perpendicular in the case of the ylides (**D** and **E**). Note that, on the one hand, the length of the ylidic bond in the case of planar cycloimmonium ylides (ylides (**A** and **B**)) is 1.42 Å. On the other hand, the negative charges found in the case of ylides (**C**, **D** and **E**) for the cyclic carbon atoms adjacent to the ylide nitrogen atom cannot be explained by the resonance interaction since the non planarity of these systems precludes such interaction. Moreover, among the eight structures available in the Cambridge Structural Data Base 1997, the shortest distance of the ylidic bond is found in the case of the ylide (**C**) (1.404 Å using X-Ray diffraction and 1.407 Å using DFT calculations). Thus, in the case of the ylides (**C** and **D**), the decrease of the ylidic bond length and the negative nature of the charges on the α carbon atoms in the pyridinium ring was attributed [51] to the Coulomb attractive strength between the aromatic positive nitrogen atom and the negative carbanion system. In the case of ylide (**E**), the α carbon atoms in the heterocyclic ring are negatively charged. Moreover, the ylidic bond is longer than the corresponding one of the ylide (**D**). In this case, neither the Coulomb attractive strength nor the resonance interaction can explain the negative nature of the charges found on the α carbon atoms in the heterocyclic ring. In order to explain these results, let us consider the bond angle described by the ylidic carbon atom and the two atoms which are directly bonded to it (other than the ylidic nitrogen atom). For the planar disubstituted cycloimmonium ylides the value of this angle for the ylide (**A**) is 119.22°, 118.31° (using X-Ray diffraction and DFT calculations, respectively), the value of the same angle for the ylide (**B**) is 119.21°, 119.83° (using X-Ray diffraction and DFT calculations, respectively). However, for the ylide (**E**), the value of this angle is (128.60°, 127.40° using X-Ray diffraction and DFT calculations, respectively). This means that there is an increase of this bond angle with respect to the corresponding one in the case of planar disubstituted cycloimmonium ylides. Thus, for the ylide (**E**), the negative charges found on the α carbon atoms in the heterocyclic ring could be explained by a field effect occurring along the space between the dipoles represented by the electron-withdrawing heteroatoms of the substituents, bonded to the ylidic carbon atom, and the α carbon atoms in the heterocyclic ring.

6. 3. Monosubstituted cycloimmonium ylides

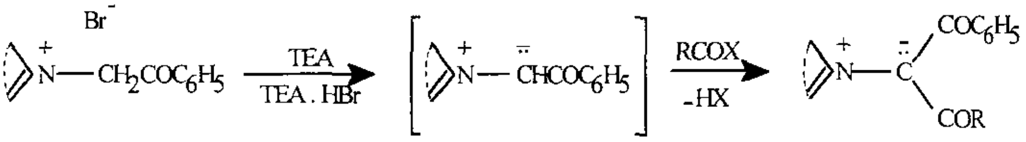
In the literature [1,2,4,5,11,65,115] there are many examples of cycloadditions where the ylides react as 1,3-dipole. Among many resonance structures of cycloimmonium ylides, the following principal structures (**17** and **18** in Scheme 12) explain the behavior of these systems as 1,3- and 1,5-dipoles as well as nucleophilic reagents, respectively. There are many reactions where the cycloimmonium ylides are involved as nucleophilic agents on the level of the ylidic carbon atom.[83,116,117]



17 **18** **19** **20**

Scheme 12 : Behavior of cycloimmonium ylides as 1,3-dipole and as 1,5-dipole.

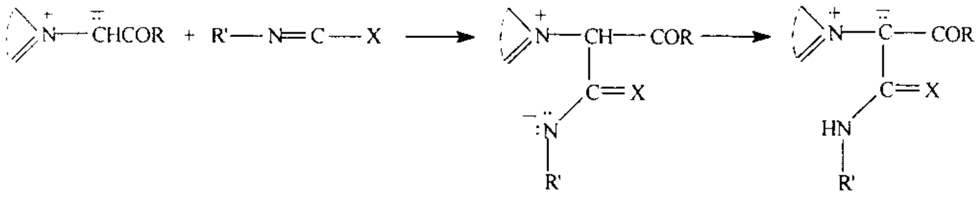
If we consider the reaction between these compounds and acyl chlorides or anhydrides [118-120] (Scheme 13), we can appreciate the pronounced nucleophilic character of monosubstituted cycloimmonium ylides.



21 **22** **23**

Scheme 13 : Nucleophilic character of monosubstituted cycloimmonium ylides.

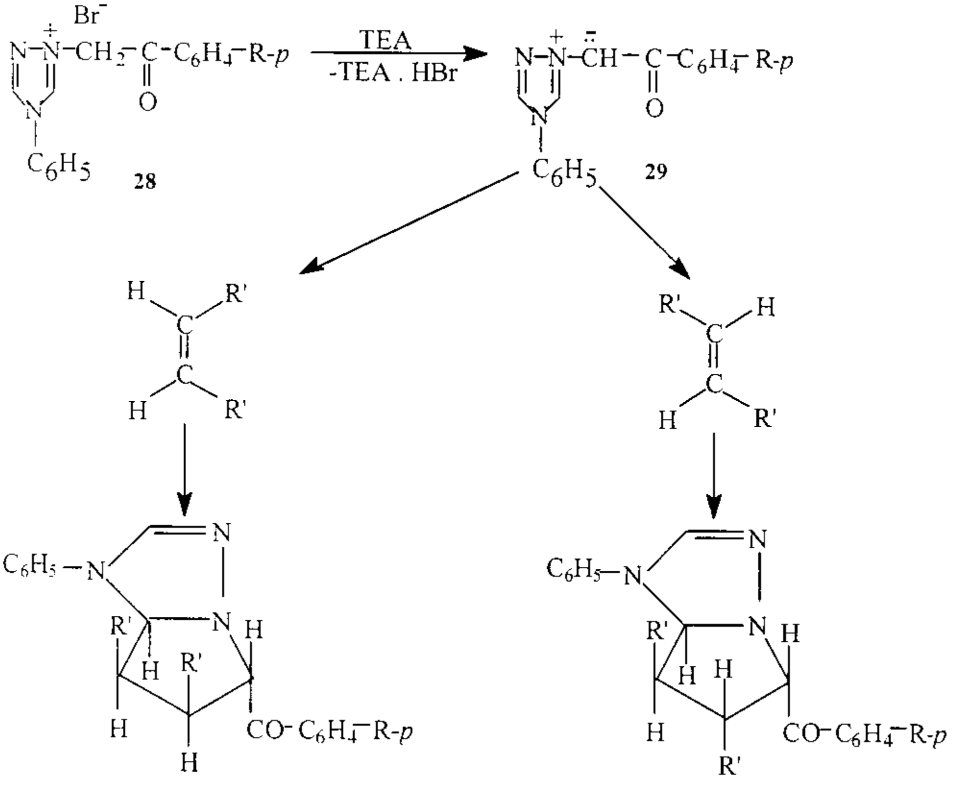
The cycloimmonium salt **(21)** reacts with triethylamine (TEA) and gives *"in situ"* the corresponding monosubstituted cycloimmonium ylide **(22)**, which reacts with acyl chlorides and anhydrides, always in basic medium, and gives the disubstituted cycloimmonium ylide **(23)**.[116] As nucleophilic agents, some monosubstituted pyridinium, isoquinolinium and 4-phenyl-1,2,4-triazolium ylides react with isocyanates and isothiocyanates giving the disubstituted cycloimmonium ylides, respectively.[90,121,122] Upon an isomerisation, the unstable intermediate **(26)** leads to the stable ylide **(27)** (Scheme 14).



X = O, S

Scheme 14 : Synthesis of disubstituted cycloimmonium ylides.

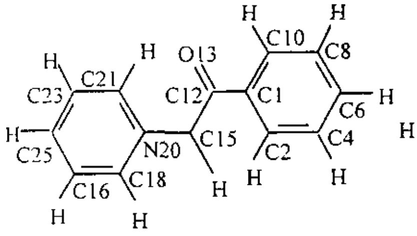
There are a lot of [3+2] dipolar cycloaddition reactions corresponding to the resonance structures of type (18), where the cycloimmonium ylides act as 1,3-dipole.[123-125] The 4-phenyl-1,3,4-triazolium phenacylides **(29)**, generated *"in situ"* from their cycloimmonium salts **(28)**, reacts with fumaric and maleic esters leading to compounds **(30 and 31)**, respectively.[126] These reactions occur stereospecifically. In IR spectra, the products have a characteristic ketonic band at 1685 cm^{-1}. Also, the NMR spectra prove these structures.[87] The remaining part of a carbonyl group reveals the 1,3-dipole character of these monosubstituted cycloimmonium ylides in such cycloadditions (Scheme 15).



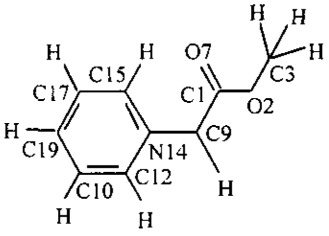
R = -OEt, -OMe, $-C_6H_5$, $-C_6H_4X$-*p* .. etc. R'= -Et, $-C_6H_5$, $-C_6H_4Me$-*p*, $-C_6H_4Me$-*o*, $-C_6H_4Br$-*p* .. etc.

Scheme 15 : Resonance structures and stereospecific reactions.

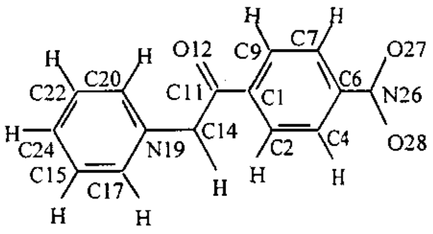
The [5+2] dipolar cycloaddition reactions where the cycloimmonium ylides act as 1,5-dipole are rarely encountered.[75] An electronic and structural study on the monosubstituted cycloimmonium ylides has been developed using semi-empirical calculations and, for the first time, DFT.[51] Note that no structure of monosubstituted cycloimmonium ylides have been resolved using X-Ray diffraction. In fact, this ylidic systems are not stable and give dimers by a [3+3] cycloaddition reaction. Theoretically, such compound should be, one day, crystallized at low temperature and in anhydric medium. Thus, the lack of X-Ray data on the monosubstituted cycloimmonium ylides, allow to consider the DFT calculations as reference in the electronic and structural study of these compounds.[51] The aim of this study was to elucidate some electronic and structural properties of the monosubstituted cycloimmonium ylides (pyridinium phenacylide, ylide **(F)**, (Scheme 16), pyridinium carbomethoxymethylide, ylide **(G)**, (Scheme 17), and the 4-nitropyridinium phenacylide, ylide **(H)**, (Scheme 18).



Scheme 16 : Ylide**(F)**.



Scheme 17 : Ylide **(G)**.



Scheme 18 : Ylide **(H)**.

The six semi-empirical methods used in the study of planar cycloimmonium ylides [46] shown that, the AM1 method, and the PM3 method to a lesser extent, have the merit to reproduce at the same time the experimental observables and the DFT results for these compounds with good accuracy. That is why only the DFT, AM1 and PM3 methods have been used in the study of the electronic and structural properties of the monosubstituted cycloimmonium ylides.[51]

Table 37 : Calculated bond lengths in Å of the ylide **(F)**.

Atom 1	Atom 2	DFT	AM1	PM3
C12	C1	1.489	1.487	1.495
C12	O13	1.264	1.253	1.236
C15	C12	1.405	1.439	1.448
C15	N20	1.370	1.366	1.365
N20	C18	1.372	1.390	1.391

N20	C21	1.375	1.382	1.388

Table 38 : Calculated bond angles in degree of the ylide **(F)**.

Atom 1	Atom 2	Atom 3	DFT	AM1	PM3
C12	C1	C10	116.65	119.52	117.03
C15	C12	C1	117.44	117.47	117.47
N20	C15	C12	124.72	124.48	126.42
C15	N20	C21	122.23	122.11	124.06
C15	N20	C18	119.61	119.81	118.78
C21	N20	C18	118.16	118.08	117.15

Table 39 : Calculated bond lengths in Å of the ylide **(G)**.

Atom 1	Atom 2	DFT	AM1	PM3
C1	O7	1.242	1.243	1.232
C9	C1	1.410	1.437	1.445
C1	O2	1.368	1.378	1.370
C9	N14	1.364	1.360	1.365
N14	C12	1.374	1.389	1.389
N14	C15	1.376	1.383	1.389

Table 40 : Calculated bond angles in degree of the ylide **(G)**.

Atom 1	Atom 2	Atom 3	DFT	AM1	PM3
C9	C1	O2	110.85	111.99	113.30
O2	C1	O7	120.93	117.19	119.04
N14	C9	C1	123.85	125.02	122.44
C9	N14	C15	122.71	123.60	121.58
C9	N14	C12	119.68	118.84	120.01
C15	N14	C12	117.61	117.55	118.40

Table 41 : Calculated bond lengths in Å of the ylide **(H)**.

Atom 1	Atom 2	DFT	AM1	PM3
C11	C1	1.490	1.493	1.501
C11	O12	1.264	1.253	1.236
C14	C11	1.402	1.433	1.442
C14	N19	1.373	1.371	1.370
N19	C17	1.370	1.388	1.389
N19	C20	1.373	1.380	1.385

Table 42 : Calculated bond angles in degree of the ylide **(H)**.

Atom 1	Atom 2	Atom 3	DFT	AM1	PM3
C14	C11	C1	117.08	117.40	117.36
C1	C11	O12	117.93	118.34	119.96
N19	C14	C11	124.65	126.06	124.26
C14	N19	C20	122.20	123.86	122.01
C14	N19	C17	119.38	118.75	119.78
C20	N19	C17	118.42	117.28	118.21

The AM1 and PM3 methods give good quality geometries when compared with those given using the DFT calculations. The DFT and semi-empirical calculations, for the ylides (**F**, **G** and **H**), show that the ylidic carbon atom and the ylidic nitrogen atom are trigonally hybridized. The sum of the bond angles around each one of these atoms is 360°. Thus, in all the geometries of the ylides (**F**, **G** and **H**), computed by semi-empirical methods or DFT technique the pyridinium ring and the carbanion are coplanar. Hence, the monosubstituted cycloimmonium ylides are planar ylidic systems. The AM1 and PM3 semi-empirical methods give good RMS for the calculated geometry with respect to the DFT data (Table 43).

Table 43 : Calculated RMS with respect to the DFT geometry (Å).

	AM1	PM3
ylide **(F)**	0.057	0.047
ylide **(G)**	0.054	0.046
ylide **(H)**	0.070	0.075

As for the disubstituted cycloimmonium ylides, the calculated charges in the case of monosubstituted cycloimmonium ylides have been discussed with a focus on the ylidic carbon atom, the ylidic nitrogen atom and the adjacent atoms, in the pyridinium ring, to the nitrogen atom that can react in [3+2] and [3+3] dipolar cycloaddition reactions, where the 1,3-dipole is considered. Otherwise, for the [5+2] dipolar cycloaddition reactions, the 1,5-dipole is considered : The α carbon atoms in the heterocyclic ring and the heteroatoms of the substituents directly bonded to the ylidic carbon atom.

Table 44 : Effective atomic charges from Mulliken populations of the ylide **(F)**.

Atom	DFT	AM1	PM3
O13	-0.496	-0.411	-0.418
C15	-0.147	-0.451	-0.834
C18	-0.106	-0.211	-0.541
N20	0.101	0.049	0.900

C21	-0.141	-0.203	-0.572

Table 45 : Effective atomic charges from Mulliken populations of the ylide **(G)**.

Atom	DFT	AM1	PM3
O7	-0.459	-0.448	-0.468
C9	-0.223	-0.429	-0.816
C12	-0.119	-0.211	-0.540
N14	0.118	0.052	0.898
C15	-0.139	-0.213	-0.576

Table 46 : Effective atomic charges from Mulliken populations of the ylide **(H)**.

Atom	DFT	AM1	PM3
O12	-0.495	-0.408	-0.411
C14	-0.144	-0.459	-0.838
C17	-0.102	-0.196	-0.527
N19	0.103	0.044	0.893
C20	-0.139	-0.190	-0.560

The *ab initio* charges given in Tables 44-46 obtained by Mulliken populations for the ylides **(F)**, **(G)** and **(H)**, respectively, show that :

- There is a good agreement between the charges of the ylides (**F**, **G** and **H**) on the level of their common atoms.

- The ylide nitrogen atoms have small positive charges : 0.101, 0.118 and 0.103 for the ylides (**F**, **G** and **H**), respectively. This shows that the positive charge is not localized on the nitrogen atom but rather is delocalized on all the atoms of the pyridinium ring. This suggests no reactivity, for the ylides (**F**, **G** and **H**), on the level of the ylidic nitrogen atom. Experimentally, as for the disubstituted cycloimmonium ylides, this atom does not interact in chemical reactions, except when the ylidic bond is broken in order to give the heterocycle and the corresponding carbene.[75,114]

- The ylide carbon atoms are negatively charged : -0.147 , -0.223 and -0.144 for the ylides (**F**, **G** and **H**), respectively. This demonstrates that the formal negative charge for the ylidic carbon atom is less delocalized in the case of monosubstituted cycloimmonium ylides than for the disubstituted cycloimmonium ylides (where the ylide carbon atoms are insignificantly charged, 0.063 in ylide **(A)** and 0.057 in ylide **(B)** [46]). Indeed, for the disubstituted cycloimmonium ylides the ylidic carbon atom has two electron-withdrawing groups, while it has only one in the case of monosubstituted cycloimmonium.

Thus, the resonance interaction phenomenon is more important only in the case of planar disubstituted cycloimmonium ylides. It is experimentally proved that the nucleophilic character of the ylidic carbon atom is bigger in the case of disubstituted cycloimmonium ylides than for the monosubstituted cycloimmonium ylides, see the reactions dependent on the substituents.[63,83,84]

- The total atomic charges of cyclic carbon atoms adjacent to the ylidic nitrogen atom have negative charges (-0.141 and -0.106 for the ylide **(F)**, -0.139 and -0.119 for the ylide **(G)** and -0.139 and -0.102 for the ylide **(H)**). The negative nature of these charges has been explained by the resonance interaction between the heterocycle and the carbanion. This precludes any nucleophlic addition on the α carbon atom in the heterocyclic ring and is in good agreement with the fact that no nucleophilic addition on such atoms has been observed.
- The oxygen atoms in the carbonyl group are negatively charged (-0.496 for the ylide **(F)**, -0.459 for the ylide **(G)** and -0.495 for the ylide **(H)**). These strong negative charges permit a strong delocalization towards the oxygen atom in the carbonyl group. This is proven by the fact that the ylides (**F**, **G** and **H**) acts as 1,5-dipole in cycloaddition reactions.

A survey of the Tables 44-46 shows that the atomic charges more comparable to those given using the DFT calculations are those calculated using the AM1 method. The charges given by the PM3 method are overestimated with respect to those of the DFT calculations.

Table 47 shows a comparison between the calculated dipole moments, using DFT, AM1 and PM3 methods, for the ylides (**F**, **G** and **H**), although the dipole moments are notoriously difficult to calculate and require extensive basis sets at the *ab initio* level.

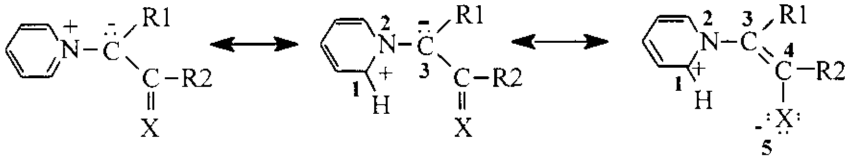
Table 47 : Calculated dipole moments (Debye).

	DFT	AM1	PM3
ylide **(F)**	4.676	3.722	3.190
ylide **(G)**	3.115	3.531	2.944
ylide **(H)**	9.827	9.056	8.149

As it was demonstrated for the disubstituted cycloimmonium ylides the dipole moment is better reproduced with the AM1 method than PM3. However, neither the charges calculated using the AM1 method nor those given using the PM3 method could explain the experimental results. The lack of the semi-empirical accuracy while compared with the DFT technique is essentially represented in reproducing a good quality charges and thus a good dipole moment. Note that the atomic charges and dipole moments more comparable to those given using the DFT calculations are those calculated using the AM1 method.

7. Reactivity of cycloimmonium ylides

Among many resonance structures of cycloimmonium ylides, the following principal structures (**33** and **34** in Scheme 19) explain the behavior of these systems as 1,3- and 1,5-dipoles as well as nucleophilic reagents, respectively.



32 **33** **34**

1,3-dipole 1,5-dipole

R1 and R2 are electron-withdrawing groups and X = O,S.

Scheme 19 : Behavior of cycloimmonium ylides as 1,3-dipole and as 1,5-dipole.

It is very important to note that no nucleophilic addition in the α position of the aromatic nitrogen atom has ever been observed. Thus, it appears to be very interesting to develop a theoretical study concerning the reactivity of cycloimmonium ylides in the context presented above i.e. to calculate the nucleophilic character on the level of the ylidic carbon atom and the 1,3-dipole in [3+2] cycloaddition reactions. There are many studies on the reactivity of cycloimmonium ylides, based on semi-empirical calculations.[4,5,63,127] Recently, a theoretical study on the reactivity of disubstituted cycloimmonium ylides, based on *ab initio* calculations, using the DFT, together with experimental results has been developed.[52] In fact, some electronic and structural properties of these compounds have been elucidated. It was also demonstrated, for the first time, that the Coulomb attractive strength is one of the principal factors responsible for the stability of cycloimmonium ylides. In addition, using the frontier molecular orbital theory, the reactivity of some virtual reaction centers by their absolute values of atomic orbital coefficients corresponding to the frontier HOMO-LUMO orbitals have been estimated. A significant difference between the planar and nonplanar cycloimmonium ylides was shown. The planar disubstituted cycloimmonium ylides seem to be ideal compounds which undergo [3+2] dipolar cycloaddition reactions. However, in the case of nonplanar disubstituted cycloimmonium ylides, the rotational barriers for the ylidic bond are higher than those of planar disubstituted cycloimmonium ylides. Also, the absolute values of atomic orbital coefficients, for the ylidic carbon atoms and the α aromatic carbon atoms, corresponding to the frontier HOMO-LUMO orbitals are smaller than those of planar disubstituted cycloimmonium ylides.

The theoretical study of the reactivity of planar and nonplanar disubstituted cycloimmonium ylides and monosubstituted cycloimmonium ylides has been developed according to the perturbation theory [128-130] of the second order for an interaction between two closed shell molecular systems A (donor) and B (acceptor). Thus, the reactivity of some virtual reaction centers by their absolute values of atomic orbital coefficients corresponding to the frontier HOMO-LUMO orbitals using the frontier molecular orbital theory [85,131] could be appreciated.

7. 1. Disubstituted cycloimmonium ylides

A theoretical study on the reactivity of the cycloimmonium ylides given in Schemes 7-11 : pyridinium dicyanomethylide [16] (ylide **A**), pyridinium carbamoylcyanomethylide [17] (ylide **B**), 2-methylaminopyridinium dinitromethylide [18] (ylide **C**), pyridinium dinitromethylide (ylide **D**) and pyridinium di-trifluoroacetylmethylide [19] (ylide **E**), respectively, has been developed using the DFT approach. The fact that the cycloaddition reactions are classified as exchange reactions allows to envisage the reactivity according to the absolute values of the atomic orbital coefficients corresponding to the frontier orbitals [52] HOMO and LUMO (Tables 48-52 for the ylides (**A**, **B**, **C**, **D** and **E**), respectively). In this way, a donor-acceptor cycloaddition reaction can be envisaged as function of the energy difference between the frontier HOMO and LUMO orbitals of the ylidic system and those corresponding to the dipolarophile.

Table 48 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide A.

Frontier molecular orbitals	Orbital energy (ev)	$2p_Z$ atomic orbital coefficients					
		C3	N4	C5	C7	N9	N11
HOMO	-5.841	0.249	0.001	0.250	-0.519	0.367	0.367
LUMO	-3.690	-0.330	0.561	-0.329	-0.255	0.234	0.235

Table 49 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **B**.

Frontier molecular orbitals	Orbital energy (ev)	$2p_Z$ of atomic orbital coefficients						
		C2	N3	C4	C7	N9	O11	N12
HOMO	-5.583	0.260	0.033	0.259	-0.578	0.401	0.234	0.245
LUMO	-3.300	-0.389	0.589	-0.315	-0.247	0.247	0.183	0.141

Table 50 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **C**.

Frontier molecular orbitals	Orbital energy (ev)	$2p_Z$ of atomic orbital coefficients						
		O4	O5	C6	C9	N11	O18	O19
HOMO	-6.164	0.292	-0.040	0.166	-0.073	-0.110	-0.289	0.120
LUMO	-3.760	-0.102	-0.065	0.002	0.338	-0.376	-0.102	-0.012

Table 51 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **D**.

Frontier molecular orbitals	Orbital energy (ev)	$2p_Z$ of atomic orbital coefficients							
		O2	O3	C4	C7	N9	C10	O17	O18
HOMO	-6.130	-0.150	-0.031	0.143	-0.024	-0.048	-0.025	-0.137	-0.200
LUMO	-4.362	-0.172	-0.095	0.093	0.201	-0.301	0.209	-0.086	-0.153

Table 52 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **E**.

Frontier molecular orbitals	Orbital energy (ev)	$2p_Z$ of atomic orbital coefficients					
		C1	O2	O3	N10	C11	C15
HOMO	-6.286	0.146	0.495	0.348	0.068	0.035	0.021
LUMO	-4.179	0.090	0.110	0.130	0.409	-0.285	-0.252

For the disubstituted cycloimmonium ylides, a great reactivity is expected where the frontier atomic orbitals coefficients corresponding to the atoms involved in the 1,3-dipole are the highest. Indeed, in the case of the ylide (**A**) the higher values are those corresponding to the atoms: C3 (0.249, -0.330), C5 (0.250, -0.329) and C7 (-0.519, -0.255) for HOMO and LUMO, respectively. In the case of the ylide (**B**) the higher values are those corresponding to the atoms: C2 (0.260, -0.389), C4 (0.259, -0.315) and C7 (-0.578, -0.247) for HOMO and LUMO, respectively. These results are in good agreement with those of the experiment where the atoms involved in [3+2] dipolar cycloaddition reactions are those reckoned by the frontier molecular orbitals theory : The ylidic carbon atom (C7 for the ylides **A** and **B**) and the α carbon atoms in the heterocyclic ring (C3 and C5 for the ylide (**A**), C2 and C4 for the ylide (**B**)). Thus, the ylides (**A** and **B**), as planar disubstituted ylidic systems, are ideal compounds which can participate in

[3+2] dipolar cycloaddition reactions by bringing closer the two parallel planes corresponding to the ylidic system and the dipolarophile. Otherwise, for the [5+2] dipolar cycloaddition reactions, there is a good agreement between the experiment and the frontier molecular orbitals theory if we consider the 1,5-dipole: The ylidic carbon atom (C7 for the ylides (**A** and **B**)) and the heteroatoms indirectly bonded to the carbanion (N9 for the ylides (**A** and **B**) and O11 for the ylide (**B**)).

However, in the case of ylides (**C**, **D** and **E**), we have not large values corresponding to the HOMO-LUMO coefficients. This is because of the non-coplanarity of the orbitals involved in the cycloaddition reactions. Thus, it is normal that these systems have to rotate on the level of the ylidic bond. The rotational barriers calculated by the DFT approach are 213.08 kcal/mol, 51.95 kcal/mol and 182.23 kcal/mol for the ylides (**C**, **D** and **E**), respectively. In these conditions, we need eventually to increase the temperature in order to permit such kind of cycloaddition reactions to happen. Note that the high value of the rotational barrier in the case of the ylide (**C**) is mainly due to the presence of the NHMe group in the α position with respect to the ylidic nitrogen atom (i.e. the steric congestion introduced by this group). Note that the high value of the rotational barrier in the case of the ylide (**E**) could be explained by a field effect occurring along the space between the dipoles represented by the withdrawing heteroatoms of the substituents, bonded to the ylidic carbon atom, and the α carbon atoms in the heterocyclic ring (see above). If we compare the rotational barriers of the ylides (**C**, **D** and **E**) with those of the ylides (**A** and **B**) (29.26 kcal/mol and 25.08 kcal/mol, respectively) we can estimate the importance of the rotational barriers on the reactivity of the nonplanar cycloimmonium ylides. A survey of Tables 50-52 show that for the ylides (**C**, **D** and **E**), the coefficients of the HOMO orbitals on the level of the α aromatic carbon atoms are smaller than those found in the case of ylides (**A** and **B**). In addition, for the ylides (**C**, **D** and **E**), the HOMO and LUMO coefficients of the ylidic carbon atoms are smaller than those of the ylides (**A** and **B**). These results suggest a small reactivity of such ylidic systems as 1,3-dipole on the level of the ylidic carbon atoms and the α aromatic carbon atoms.

7. 2. Monosubstituted cycloimmonium ylides

A theoretical study on the reactivity of the cycloimmonium ylides given in Schemes 16-18 : [pyridinium phenacylide, ylide (**F**), pyridinium carbomethoxymethylide, ylide (**G**), and the 4-nitropyridinium phenacylide, ylide (**H**), respectively] has been developed using the DFT approach.[52] As for the disubstituted cycloimmonium ylides the reactivity of the monosubstituted cycloimmonium ylides has been envisaged according to the absolute values of the atomic orbital coefficients corresponding to the frontier orbitals [52] HOMO and LUMO (Tables 53-55 for the ylides (**F**, **G** and **H**), respectively).

Table 53 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **F**.

Frontier molecular orbitals	Orbital energy (Ha)	$2p_Z$ of atomic orbital coefficients						
		C6	C12	O13	C15	C18	N20	C21
HOMO	-5.199	0.122	0.157	-0.402	0.577	-0.291	-0.021	-0.285
LUMO	-3.107	-0.193	-0.304	0.344	-0.158	-0.373	0.528	-0.301

Table 54 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **G**.

Frontier molecular orbitals	Orbital energy (Ha)	$2p_Z$ of atomic orbital coefficients					
		O2	O7	C9	C12	N14	C15
HOMO	-4.973	0.271	0.307	-0.615	0.315	0.020	0.309
LUMO	-2.732	0.209	0.288	-0.309	-0.370	0.606	-0.283

Table 55 : Atomic charges, atomic orbital coefficients and frontier molecular orbital energies of ylide **H**.

Frontier molecular orbitals	Orbital energy (Ha)	$2p_Z$ of atomic orbital coefficients					
		C11	O12	C14	C17	N19	C20
HOMO	-5.649	0.162	-0.434	0.574	-0.280	-0.033	-0.275
LUMO	-3.941	0.174	-0.232	-0.064	0.207	-0.215	0.191

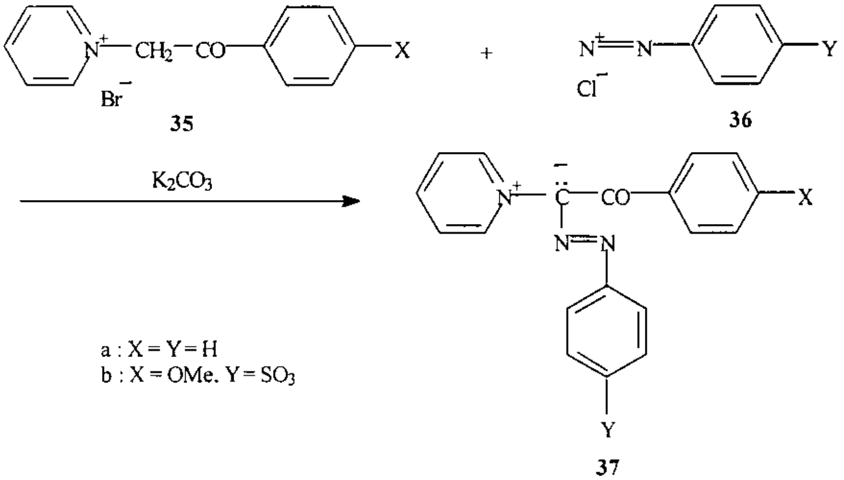
In the case of monosubstituted cycloimmonium ylides a great reactivity is expected where the frontier atomic orbitals coefficients corresponding to the atoms involved in the 1,3-dipole are the highest. Indeed, for the ylide **(F)** the higher values are those corresponding to the atoms : C15 (0.577, -0.158), C18 (-0.291, -0.373), C21 (-0.285, -0.301) and O13 (-0.402, 0.344) for HOMO and LUMO, respectively. In the case of the ylide **(G)** the higher values are those corresponding to the atoms : C9 (-0.615, -0.309), C12 (0.315, -0.370), C15 (0.309, -0.283) and O7 (0.307, 0.288) for HOMO and LUMO, respectively. In the case of the ylide **(H)** the higher values are those corresponding to the atoms: C14 (0.574, -0.064), C17 (-0.280, 0.207), C20 (-0.275, 0.191) and O12 (-0.434, -0.232) for HOMO and LUMO, respectively. These results are in good agreement with those of the experiment where the atoms involved in [3+2] dipolar cycloaddition reactions are those reckoned by the frontier molecular orbitals theory : The ylidic carbon atom (C15 for the ylide **(F)**, C9 for the ylide **(G)** and C14 for the ylide **(H)**) and the α carbon atoms in the heterocyclic ring (C18 for the ylide **(F)**, C12 for the ylide **(G)** and C17 for the ylide **(H)**). Thus, the ylides (**F**, **G** and **H**), as planar monosubsituted ylidic systems, are ideal compounds which can participate in [3+2] dipolar cycloaddition reactions by bringing closer the two parallel planes corresponding to the ylidic system and the dipolarophile. The 1,3-dipole is represented by the ylidic carbon atom and the α carbon atoms in the heterocyclic ring. Otherwise, for the [5+2] dipolar cycloaddition reactions, there is a good agreement between the experiment and the frontier molecular orbitals theory if we consider the 1,5-dipole. Note that the frontier atomic orbitals coefficients corresponding to the ylidic nitrogen atom are : N20 (-0.021, 0.528) for the ylide **(F)**, N14 (0.020, 0.606) for the ylide **(G)** and N19 (-0.033, -0.215) for the ylide **(H)** for HOMO and LUMO, respectively. Thus, for the ylidic nitrogen atom, the atomic orbitals coefficients corresponding to the HOMO orbital are very low. This is in good agreement with the experiment where the ylidic nitrogen atom does not participate in [3+2] *dipolar cycloaddition* reaction. It is very interesting to remark that in the case of the monosubstituted cycloimmonium ylides, (**F**, **G** and **H**), the frontier atomic orbitals coefficients (HOMO) corresponding to the α aromatic carbon atoms in the pyridinium ring and the ylidic carbon atom are greater than those of the planar disubstituted cycloimmonium ylides, (**A** and **B**). These results are in good agreement with the experiment, where it has been proved that the nucleophilic character of the ylide carbon atom is bigger in the case of monosubstituted cycloimmonium ylides than for the disubstituted cycloimmonium ylides, see the reactions dependent on the substituents.[63,83,84] These results are also in good agreement with the Mulliken scheme (as discussed in the stability of cycloimmonium ylides within this report) and the frontier atomic orbital theory. In fact, on the one hand, the ylide carbon atoms are negatively charged : -0.147 , -0.223 and -0.144 for the ylides (**F**, **G** and **H**), respectively. This demonstrates that the formal negative charge for the ylidic carbanion atom is less delocalized in the case of monosubstituted cycloimmonium ylides than for the disubstituted cycloimmonium ylides (where the ylide carbon atoms are insignificantly charged, 0.063 in ylide **(A)** and 0.057 in ylide **(B)**.[46] Thus, the resonance interaction phenomenon is favored only in the case of planar disubstituted cycloimmonium ylides. On the other hand, the frontier atomic orbitals coefficients corresponding to the ylidic carbon atom are : C15 (0.577, -0.158) for the ylide **(F)**, C9 (-0.615, -0.309) for the ylide **(G)**, C14 (0.574, -0.064) for the ylide **(H)**, for HOMO and LUMO, respectively. The same coefficients in the case of the ylides (**A** and **B**) are : C7 (-0.519, -0.255) et C7 (-0.578, -0.247), for HOMO and LUMO, respectively. The rotational barriers calculated by the DFT approach are 26.11 kcal/mol, 26.62 kcal/mol and 26.22 kcal/mol for the ylides (**F**, **G** and **H**), respectively.[52] These rotational barriers are comparable with those of the planar disubstituted cycloimmonium ylides (29.26 kcal/mol and 25.08 kcal/mol, for the ylides **(A)** and **(B)**, respectively).[46] This is in good agreement with the experiment where these compounds have the same reaction affinity in the dipolar cycloaddition reactions.

From the total atomic charges, one could infer that the following atoms : O13 (-0.226), C25 (-0.306) for the ylide **(F)**, O7 (-0.459), O2 (-0.367), C3 (-0.712), C19 (-0.319) for the ylide **(G)**, C24 (-0.300), O12 (-0.495) for the ylide **(H)**, are more reactive than the ylide carbon atom : C15 (-0.147) for the ylide **(F)**, C9 (-0.223) for the ylide **(G)** and C14 (-0.144) for the ylide **(H)**. From the atomic orbital coefficients we conclude that the same atoms for the ylides **(F)**, **(G)** and **(H)** are less reactive than the ylide carbon atom. The $2p_Z$ atomic orbital coefficients corresponding to the HOMO orbitals of the ylide carbon atoms are the highest. Thus the heteroatoms in the position 5 (Scheme 19) in the 1,5-dipole are less reactive than the ylidic carbon atom which is in the position 3 in the 1,3-dipole. This is in good agreement with the experiment since it explain why the 1,5-dipolar cycloaddition reactions are more rarely encountered than the 1,3-dipolar cycloaddition reactions.

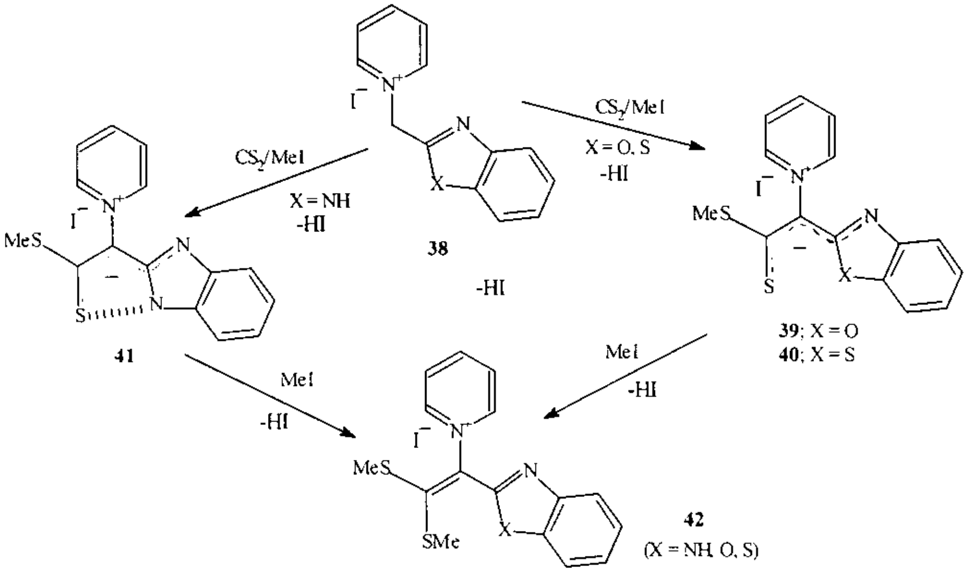
The results summarized above on the reactivity of cycloimmonium ylides, based on the DFT approach, emphasize the following principal and fundamental features of cycloimmonium ylides : The positive charge generally attributed to the ylide nitrogen atom is never high and is delocalized. The negative charges found for the cyclic carbon atoms adjacent to the ylide nitrogen atom precludes any nucleophlic addition on the α carbon atoms in the heterocyclic ring. This is in good agreement with the experiment, where no nucleophilic addition on such atoms has ever been observed. The formal negative charge often accepted for the ylidic carbanion is too small and is also strongly delocalized. For the first time, it has been demonstrated that the resonance interaction and the Coulomb attractive strength are principal factors in the stability of cycloimmonium ylides.[46,51] Indeed, the ylidic bond in the case of ylide **(D)** (nonplanar cycloimmonium ylide) is found to be less than the one of planar cycloimmonium ylides (ylides **A** and **B**). Moreover, the total atomic charges corresponding to the ylides (**A**, **B**, **D** and **E**) are comparable on the level of the ylidic aromatic nitrogen atoms, the ylidic carbon atoms and the carbon atoms in the heterocyclic ring. The planar ylidic systems (ylides **A** and **B**) are ideal compounds which undergo [3+2] dipolar cycloaddition reactions by bringing closer the two parallel planes corresponding to the ylidic system and the dipolarophile. In this case, a great reactivity for the atoms involved in the 1,3-dipole is obtained. The frontier atomic orbital coefficients corresponding to these atoms, are the highest. For nonplanar ylidic systems (ylides **C**, **D** and **E**) the $2p_Z$ atomic orbital coefficients corresponding to the HOMO orbitals on the level of the α aromatic carbon atoms and the ylidic carbon atoms are less than those found in the case of planar ylidic systems (ylides **A** and **B**). Moreover the rotational barriers, of the ylidic bond, in the nonplanar disubstituted cycloimmonium ylides are higher than those corresponding to the planar disubstituted cycloimmonium ylides. These suggest a small reactivity of such nonplanar ylidic systems as 1,3-dipole in [3+2] dipolar cycloaddition reaction. Thus, only an increase of the temperature will allow such kind of cycloaddition reactions to occur. Therefore, the reaction course must be strongly controlled by the reaction conditions like solvent and reagents. The high density of charges and the high frontier atomic orbital coefficients (HOMO) found on the ylidic carbon atom prove that the monosubstituted cycloimmonium ylides are nucleophilic agents more reactive, on the level of this atom, than the disubstituted cycloimmonium ylides. This is due to their low rotational barriers and to the existence of the resonance interaction phenomenon in the disubstituted cycloimmonium ylides. This tends to minimize the negative charge and the frontier atomic orbital coefficients of the ylidic carbon atom. Thus, the monosubstituted cycloimmonium ylides may undergo [3+2] dipolar cycloaddition reactions more rapidly than the disubstituted cycloimmonium ylides.

8. Cycloimmonium ylides as nucleophilic agents

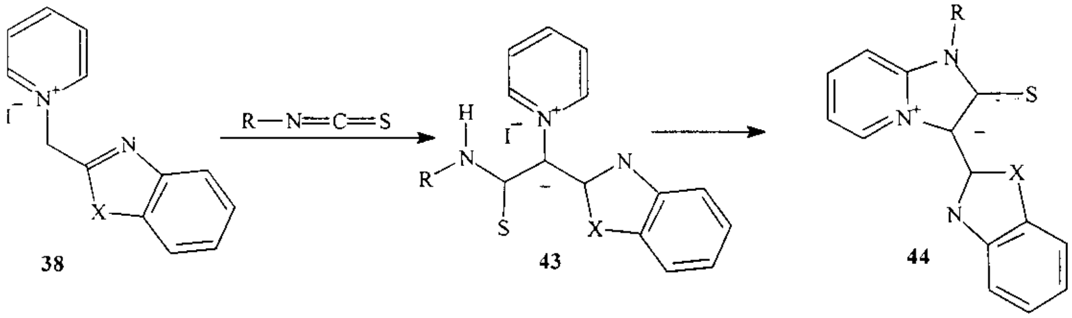
The pyridinium ylides **(35)** react with the diazonium salts **(36)** giving the intensive colored disubstituted ylides **(37)**.[132] The same reactions are observed with 1,3,4-triazolium ylides.[133]



The N-[2-(1,3-benzazolyl)]pyridinium ylide **(38)** generated *in situ* in salt reacts with carbon disulfide, isothiocyanate derivatives, phenylisocyanate and benzoyl chloride giving the corresponding disubstituted carbanion ylides e. g. **(39-41)**.[134] The compounds **(39-41)** reacts with methyliodide giving the final product **(42)** by an hydroiodide elimination.[134]

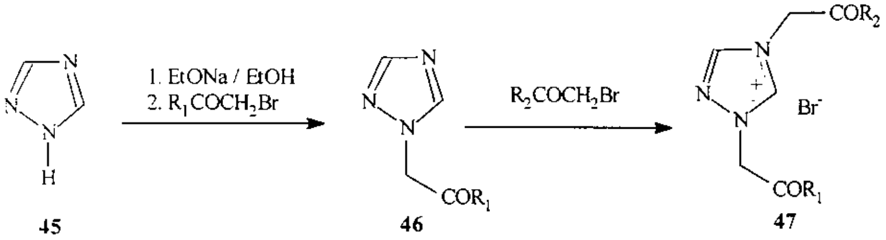


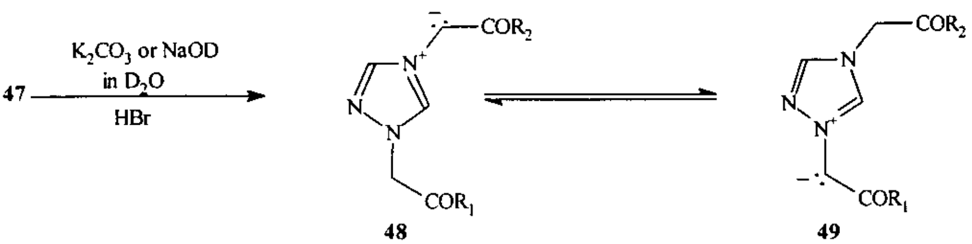
Sometimes, more differently chemical path way could be observed.



(X = NH, O, S) (X = NH; not isolable) (X= NH)

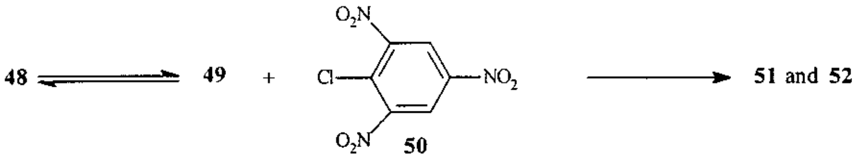
The monitoring by ^{1}H NMR of the kinetics of the tautomeric equilibrium between the triazolium ylides **(49 f-h)** and **(50 f-h)** confirms the existence of a dynamic equilibrium and corroborates the results obtained by the chemically induced perturbation of the equilibrium.[117]

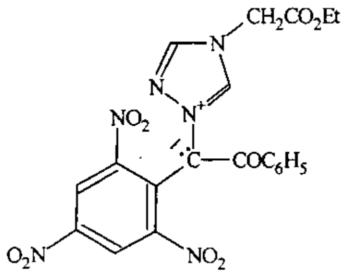




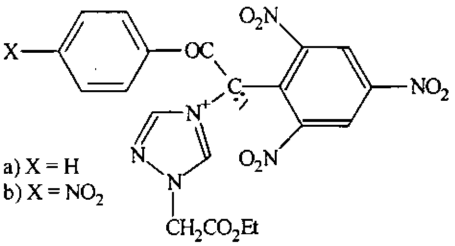
	R_1	R_2		$R_1 = R_2$
a	C_6H_5	EtO	f	C_6H_5
b	EtO	C_6H_5	g	p-MeC_6H_4
c	EtO	p-$NO_2C_6H_4$	h	p-$MeOC_6H_5$
d	C_6H_5	p-$NO_2C_6H_4$	i	p-$NO_2C_6H_4$
e	p-$NO_2C_6H_4$	C_6H_5		

Always, the picryl chloride (**50**) reacts only with the phenacylide ylidic form.[86,135]





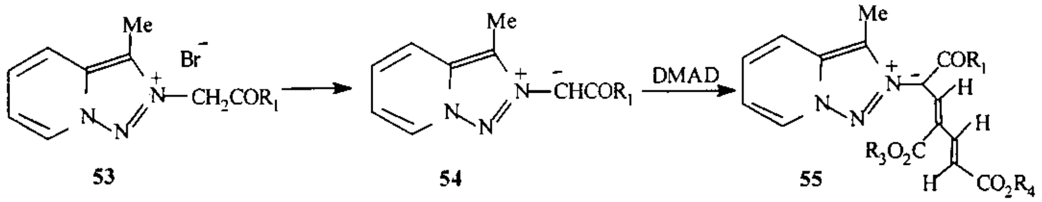
51

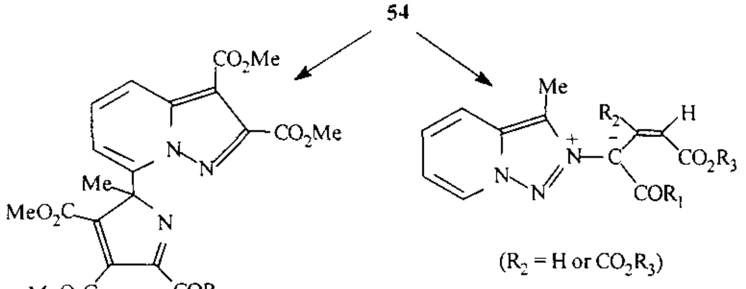


a) X = H
b) X = NO_2

52

A remarkable rearrangement[136] during reaction between triazolopyridinium ylides and dimethyl acetylenedicarboxylate (DMAD) has been observed. The ylides (**54**) obtained in 2-acylmethyltriazolopyridinium salts (**53**), react with dimethyl acetylenedicarboxylate in toluene to give the 7-pyrrolpyrazol[1,5-*a*]pyridines (**57**) and the corresponding open ylides (**55**) and (**56**).



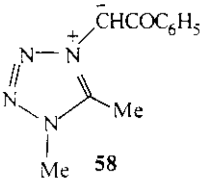


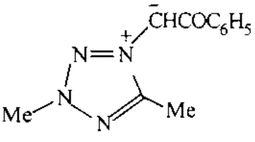
$(R_2 = H \text{ or } CO_2R_3)$

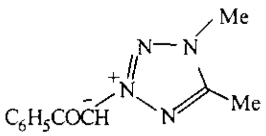
57 **56**

throughout a : $R_1 = OMe$, b : $R_1 = OEt$, c : $R_1 = C_6H_5$, $R_3 = R_4 = Me$

Various 1-alkyl-5-methyl-1*H*-tetrazolium-4-phenacylides have been prepared, acylated and thiocarbamoylated.[137] The unstable ylide **(60)** has been acylated *in situ*.

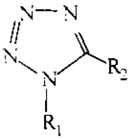

58

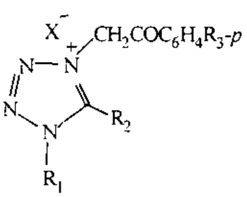

59

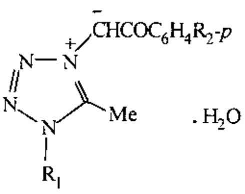

60

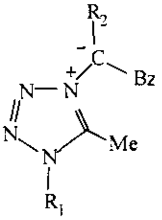
The synthetic route was the general method of Kröhnke,[138-140] i.e. the treatment of the corresponding tetrazolium salts with excess of potassium carbonate in the cold while compounds **(58)** and **(59)** were obtained as reasonably stable solids. The isomer **(60)** was an oil that decomposed on isolation.

The cycloimmonium ylides **(60)** generated *in situ* in theirs cycloimmonium salts react with acetic and benzoic anhydrides or with isocyanates and isothiocyanates giving the disubstituted carbanion ylides of type **(64)**.


61


62


63


64

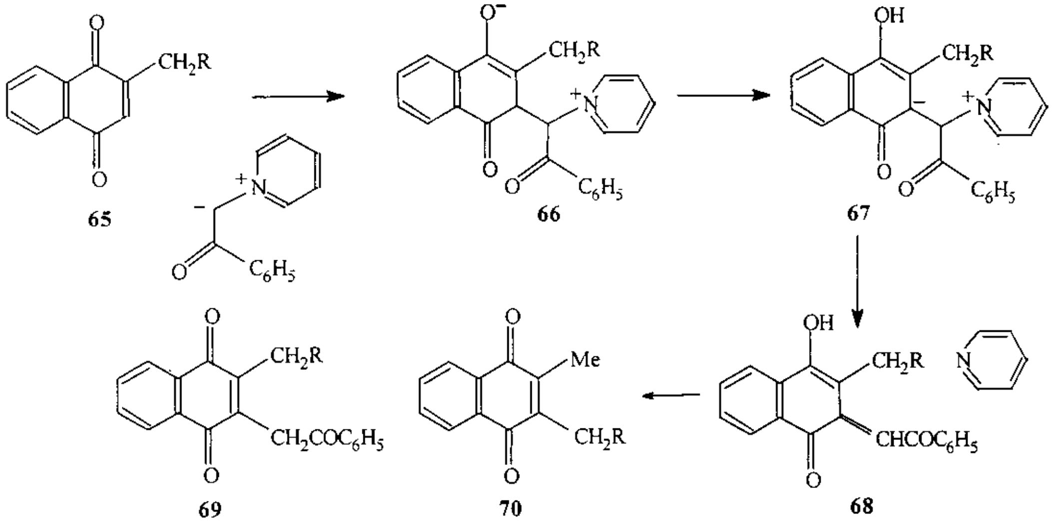
61a : $R_1 = R_2 = Me$
61b : $R_1 = Pr$, $R_2 = Me$
61c: $R_1 = Pr\text{-}i$, $R_2 = Me$
61d : $R_1 = Bu\text{-}i$, $R_2 = Me$
61e : $R_1 = CH_2Bu\text{-t}$, $R_2 = Me$
61f : $R_1 = c\text{-}C_6H_{11}$, $R_2 = Me$
63a : $R_1 = Me$, $R_2 = Br$
63b : $R_1 = Me$, $R_2 = NO_2$
63c: $R_1 = Pr$, $R_2 = H$

62a : $R_1 = R_2 = Me$, $R_3 = Br$, $X = Br$
62b : $R_1 = R_2 = Me$, $R_3 = NO_2$, $X = Br$
62c : $R_1 = Pr$, $R_2 = Me$, $R_3 = H$, $X = Br$
62d : $R_1 = Pr\text{-}i$, $R_2 = Me$, $R_3 = H$, $X = Br$
62e : $R_1 = Bu\text{-}i$, $R_2 = Me$, $R_3 = H$, $X = Br$
62f : $R_1 = CH_2Bu\text{-}t$, $R_2 = Me$, $R_3 = H$, $X = Br$
64a : $R_1 = Me$, $R_2 = Ac$
64b : $R_1 = Me$, $R_2 = CH_2C_6H_5$
64c : $R_1 = Bu\text{-}i$, $R_2 = CH_2C_6H_5$

63d : R_1 = Pr-*i*, R_2 = H
63e : R_1 = Bu-*i*, R_2 = H
63f : R_1 = CH_2Bu-*t*, R_2 = H

64d : R_1 = *c*-C_6H_{11}, R_2 = $CH_2C_6H_5$
64e : R_1 = *c*-C_6H_{11}, R_2 = $CONHC_6H_5$
64f : R_1 = Bu-*t*, R_2 = $CSNHC_6H_5$

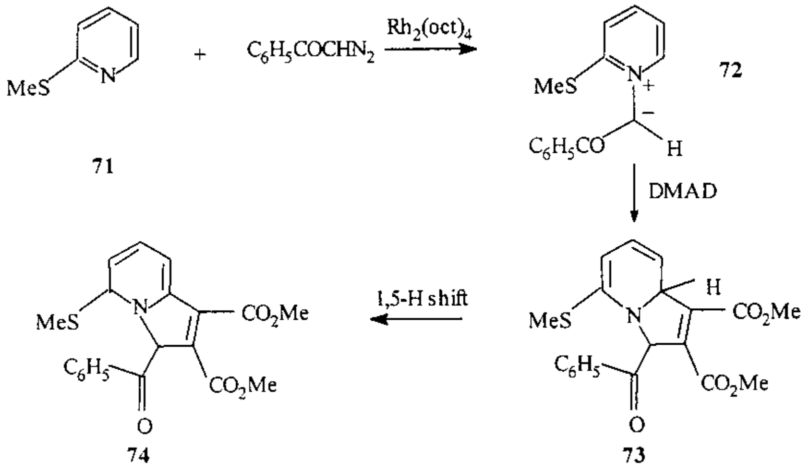
Improvements have been made in the use of acylated pyridinium ylides for the transformation of 2-methyl-1,4-naphthoquinone into derivatives of 2,3-disubstituted 1,4-naphthoquinone.[141]



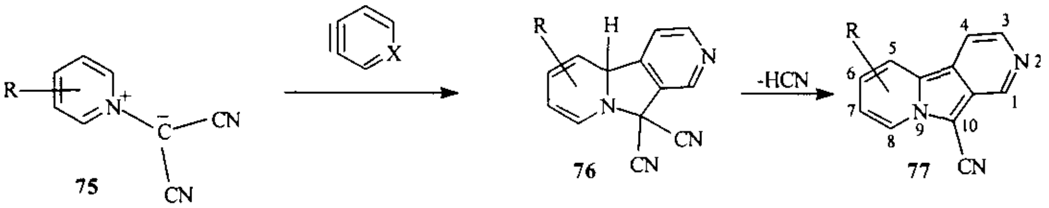
R = H, Me, OMe, CO_2Me, CN

9. Cycloimmonium ylides as dipolarophiles

The reaction of α-diazoacetophenone with 2-methylthiopyridine **(71)** in the presence of 1,2 equiv. of DMAD gave 3-benzoyl-1,2-dicarbomethoxy-3,5-dihydro-5-methylthioindolizine **(72)** in 60 % yield.[142] As catalytic agent the rhodium (II) octanoate is used.

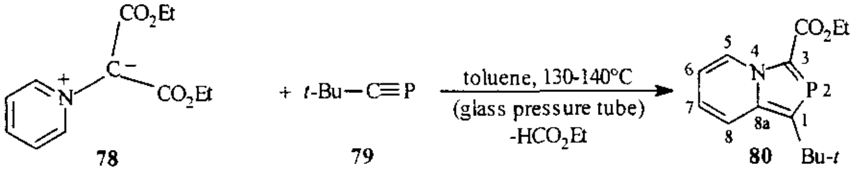


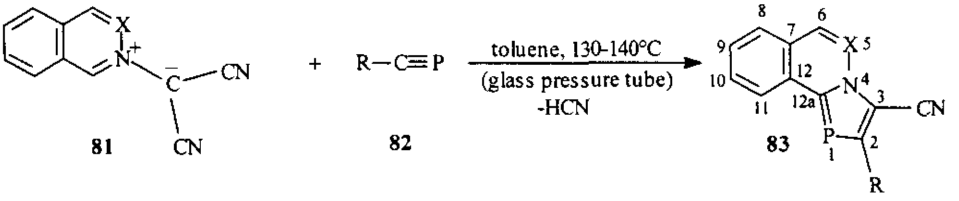
Dicyanomethylides (**75**) with benzyne (X = CH), afforded 10,10-dicyanobenz[*a*]indolizine (**76**, X = CH) together with the dibenzo[2.2.3]cyclazines (**77**, X = CH).[144-145] The same ylides with 3,4-dehydropyridine (X = N) generated in 3-(3',3''-dimethyltriazen-1-yl)pyridine-4-carboxylic acid gave the dehydrocyanated pyridoindolizine product (**77**, X = N).[143]



R = H, 4-Me, 3,5-diMe, 4-Ac, 3-Me

The cycloimmonium ylides such as the compounds (**78**) and (**81**) in which the nitrogen atom is incorporated in a six-membered heterocyclic ring undergo regiospecific [3+2] cycloadditions with the phosphaalkynes (**79**) and (**82**) at 130-140°C to furnish the phosphaindolizines (**80**) and (**83**) after elimination of ethyl formate or hydrogen cyanide, respectively.[147]



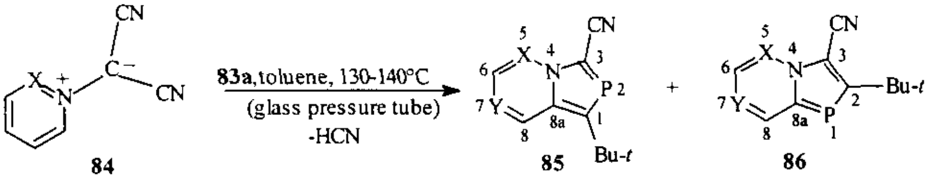


81a : X = CH
81b : X = N

82a : X = Bu-*t*
82b : X = CMe_2Et

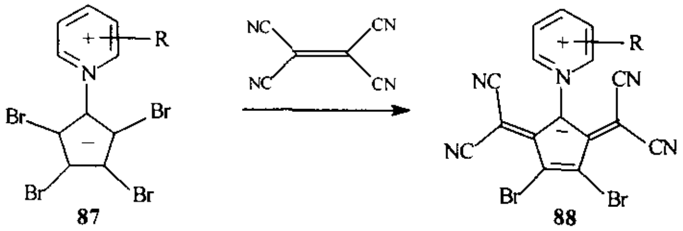
83a : X = CH, R = Bu-*t*
83b : X = N, R = Bu-*t*
83c : X = CH, R = CMe_2Et

In contrast, dipoles of the type (**84**) react unspecifically with the phosphaalkyne (**79**) to yield the regioisomers (**85**) and (**86**).



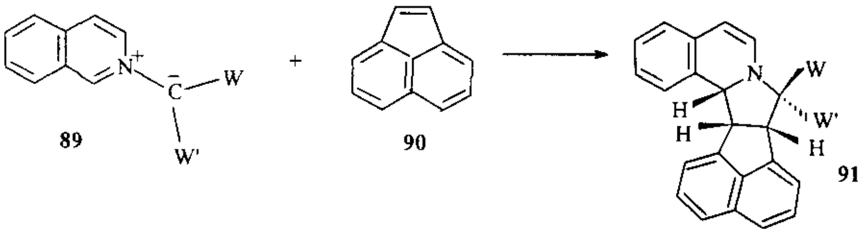
84-86	a	b	c	d	e	f	g	h	i
X	CH	N	CH	CH	CH	CH	CH	CH	CH
Y	CH	CH	N	CMe	CBu-*t*	CPr-*i*	C-CO_2Me	C-CN	C-COC_6H_5

A very interesting reaction occur between tetrabromo pyridinocyclopentadienides **(87)** and tetracyanoethylene.[147]



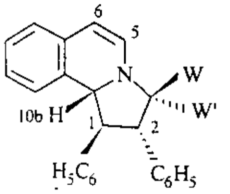
R = H, 4-Me, 3-Me, 2-Me, 4-OMe, 4-CO_2Me, 3-CO_2Me, 4-CN, 4-$NHMe_2$

The disubstituted isoquinolinium ylides **(89)** with acenaphthylene as a symmetrically aryl-substituted cyclic olefin produced the cycloadducts **(91)** of *endo* and *exo* structures.[148]

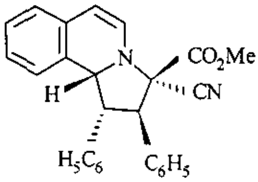


W = W' = CO_2Me ; W = W' = CN ; W = CO_2Me, W' = CN

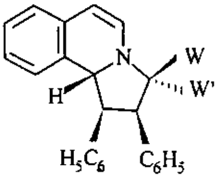
Similar reaction of ylides **(89)** with *E*- and *Z*-stilbenes produced *E*- **(92-94)** and *Z*-cycloadducts **(96)** and **(97)**, respectively.



92 W = W' = CO_2Me
93 W = W' = CN
94 W = CO_2Me, W' = CN

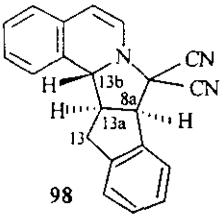


95

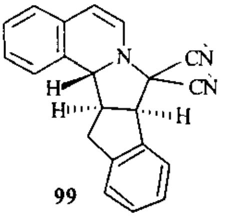


96 W = W' = CN
97 W = CO_2Me, W' = CN

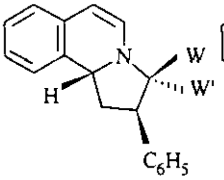
The cycloadducts **(96)** and **(97)** to *Z*-stilbene bear *trans* diaxial stereochemistry between 1-H and 10b-H and are assigned to be the exo-cycloadducts. Ylides **(89)** react with such unsymmetrically aryl-substituted



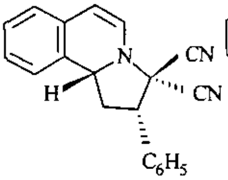
98



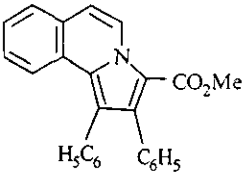
99



100



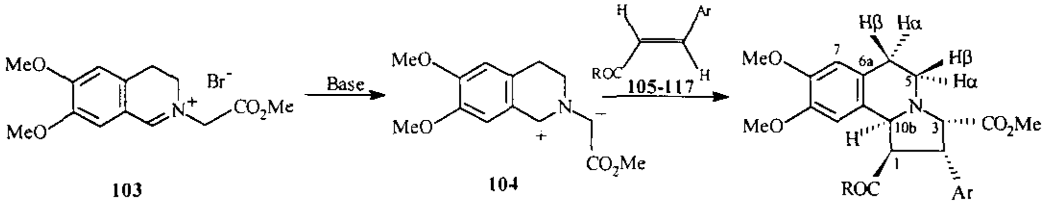
101



102

olefins as inolene and styrene giving endo and exo cycloadducts.

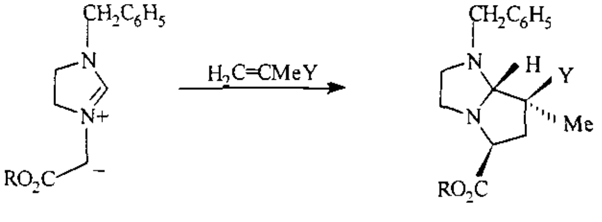
The *N*-methoxycarbonylmethyl-3,4-dihydro-6,7-dimethoxyisoquinolinium bromide **(103)** reacts with some substituted alkenes giving generally *endo* type cycloadducts.[149]



103 **104** **118-131**

	R	Ar
105,118	-OMe	-C_6H_5
106,119	-OMe	-$C_6H_4(NO_2)$-*p*
107,120	-OMe	-$C_6H_4(NO_2)$-*p*
108,121	-OMe	-C_6H_5Me-*p*
109,122	-OMe	3',4',5'- trimethoxyphenyl
110,123	-OMe	thienyl
111,124	-OMe	α-furyl
112,125	-Me	-$C_6H_5(OCHO)$-3,4
113,126	-Me	α-furyl
114,127	-C_6H_5	-C_6H_5
115,128	-C_6H_5	-$C_6H_4(NO_2)$-*p*
116,129	-C_6H_5	α-furyl
117,130,131	-$C_6H_4(NO_2)$-*p*	α-furyl

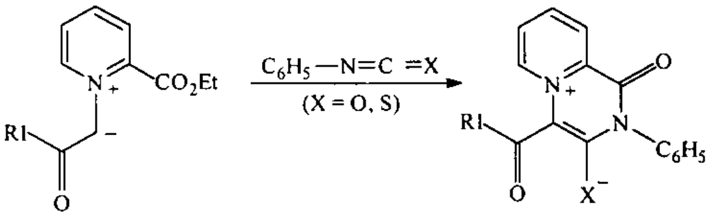
1,3-Dipolar cycloadditions of 4,5-dihydroimidazolium ylides **(132)** formed from 1-benzyl-4,5-dihydroimidazole proceed *via* a convenient one-step, one-pot protocol to give hexahydropyrrolo[1,2-*a*]-imidazole esters.[150]



132 **133**

On the 1,3-dipolar cycloadditions of cycloimmonium ylides, the microwave irradiation in solvent free conditions,[151] the use of a solid-liquid phase-transfer system,[152] or a new oxidant tetrapyridine cobalt (II) dichromate [153] as well as the use of benzyne, [154] 1,2,3-triphenylcyclopropene [155] and cyclooctyne[156,157] as dipolarophiles are some very interesting aspects concerning the chemistry of ylides.

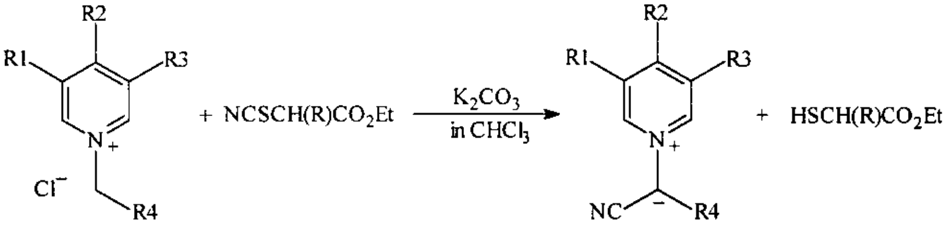
Particularly by cycloaddition reactions of pyridinium ylides, new complex polycyclic compounds have been reported. [158,159] Rarely, the cycloimmonium ylides **134** react as 1,4-dipole with phenyl isocyanate and isothiocyanate giving more complex heterocyclic compounds **135**. [160]



134 **135**

R1 = OEt, C_6H_5

Various pyridinium monosubstituted methylides, generated *in situ* from the corresponding salts **136**, were smoothly attacked to the cyano group in ethylthiocyanatoacetate or ethyl 2-thiocyanatopropionate to afford the corresponding pyridinium substituted cyanomethylides **138** in low to moderate yields.[161]



136 **137a, b** **138** **139a, b**

137a, 139a : R = H ; **137b, 139b** : R = Me

136,138	R1	R2	R3	R4	Yield (%)
a	H	H	H	CN	7 (3)
b	H	Me	H	CN	15 (4)
c	Me	H	Me	CN	18 (7)
d	H	H	H	CO_2Et	63
e	H	Me	H	CO_2Et	53
f	Me	H	M	CO_2Et	51

136,138	R1	R2	R3	R4	Yield (%)
g	H	H	H	COMe	58
h	H	Me	H	COMe	40
i	Me	H	Me	COMe	42
j	H	H	H	COC_6H_5	45
k	H	Me	H	COC_6H_5	37
l	Me	H	Me	COC_6H_5	28

Note that the yield in the parenthesis is for the reaction using **137b**.

The ^{13}C, ^{14}N and ^{15}N chemical shifts and shielding changes (SCS) of ylidic carbons and nitrogens in 4-substituted pyridinium dicyanomethylides[162, 163] are given in Tables 56 and 57.

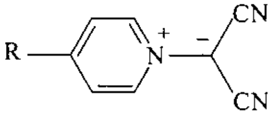
Table 56 : Chemical shift of pyridinium carbon and nitrogen of compounds **140**.

R	CN	CO_2Me	COMe	COC_6H_5	H	$CH_2C_6H_5$	Bu-*t*	Pr-*i*	Et	Me
^{13}C	62.1	60.3	60.03	-	58.4	-	57.7	57.6	57.6	57.2
^{15}N	154.1	154.4	155.0	156.1	162.3	167.4	167.9	167.8	167.8	162.3
^{15}N (N^+)	153.9	153.9	155.0	155.6	161.4	166.9	167.7	167.6	167.9	168.5
^{15}N (CN)	88.3	88.5	88.8	88.6	89.0	88.8	89.1	89.2	89.0	89.0

Table 57 : SCS values of ylidic carbon and pyridinium nitrogen of compounds **140**.

R	CN	CO_2Me	COMe	COC_6H_5	H	$CH_2C_6H_5$	Bu-*t*	Pr-*i*	Et	Me
^{13}C (1)	-3.7	-1.9	-1.9	-2.2	0	0.9	0.7	0.8	0.8	1.2
^{15}N (2)	-7.5	-7.5	-6.4	-5.8	0	5.5	6.3	6.2	6.5	7.1
^{15}N (3)	-10.1	-	-11.7	-10.7 (4)	0	6.7	5.8	5.9	6.6	8.0

(1) The positive values show the upfield shifts. (2) The SCS of compounds **140**. (3) The SCS of a nitrogen of pyridines calculated from data in paper.[164] (4) data in paper.[163]



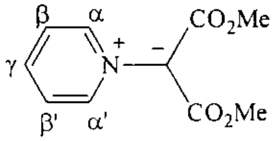
140

A linear correlation between the ^{13}C-SCS and the ^{15}N-SCS, taking into account substituent constants, has been obtained:

$$^{13}C\text{-SCS} = 0.25(^{15}N\text{-SCS}) - 0.66 \qquad r = 0.956 \text{ (r is the correlation factor)}$$

It is concluded that shielding of the ylidic ^{15}N and ^{13}C nuclei is governed by the analogous influences due to the substituents R. Whereby, on the ppm scale, the nitrogen chemical shift is four times more sensitive towards substituents than the carbon shift.

By means of ESR spectroscopy, it was found that short-lived anion radicals of pyridinium bis(alkoxycarbonyl)methylide **141** have unusual hyperfine splitting (hfs) and a unique unsymmetrical electronic structures.[165, 166]



141

Table 58 : Observed hfs constants a_H and a_D and their ratio in (gauss)[a] of anion radical of compound **141** and its deuterated derivative **141**-d4 in THF at room temperature.

Position	**141**	**141**-d4	a_D/a_H
N	5.45	5.44	
α	3.30	0.52[b]	0.1576
α'	2.12	0.33[b]	0.1557
β	1.51	0.23[b]	0.1523
β'	0.90	0.14[b]	0.1556
γ	3.61	3.67	

[a] 1 gauss = 10^{-4} tesla. [b] Values of the hfs constants of the deuterons (note that an active γ-deuteron of the pyridine ring was converted to a proton during the formation of the anion radical).

The short-lived anion radical has been obtained from ylide solved in degassed THF and sodium metal. Finally, by photoacoustic calorimetry have been determined the enthalpies of reaction between methyl and phenylchlorocarbenes with substituted pyridines.[167]

REFERENCES

1. A. W. Johnson, Ylide chemistry, Academic press, New York, 1966.
2. I. Zugravescu and M. Petrovanu, N-Ylide Chemistry, Mc Graw Hill, New York, 1976.
3. I. Zugravescu and M. Petrovanu, Chimia N-ilideor, Editura Academici, Bucuresti, 1974.
4. G. Surpateanu, J. P. Catteau, P. Karafiloglou, and A. Lablache-Combier, *Tetrahedron*, 1976, **32**, 2647.
5. G. Surpateanu and A. Lablache-Combier, *Heterocycles*, 1984, **22**, 2079.
6. M. Petrovanu, G. Surpateanu, and I. Zugravescu, *Acad. Repub. Soc. Rom.*, 1985, **6**, 89 [*Chem. Abstr.*, 1985, **105**, 133769r].
7. G. Surpateanu and E. Rucinschi, *Chem. Anal.*, 1974, **19**, 493 [*Chem. Abstr.*, 1974, **82**, 25391j].
8. G. Surpateanu, N. Foca, and I. Zugravescu, *An. Stiint. Univ. Iasi*, 1973, **19**, 39 [*Chem. Abstr.*, 1973, **79**, 121641z].
9. G. Surpateanu, V. Stefan, E. Rucinschi, and I. Zugravescu, *Phys. Status Solidi (A)*, 1970, **3**, k147 [*Chem. Abstr.*, 1970, **74**, 26098r].
10. G. Surpateanu, V. Stefan, E. Rucinschi, and I. Zugravescu, *An. Stiint. Univ. Iasi*, 1974, **20**, 71 [*Chem. Abstr.*, 1974, **82**, 148737j].
11. A. Padwa, 1,3-Dipolar Cycloaddition Chemistry, Wiley Interscience, New York, 1984.
12. M. Petrovanu and I. Zugravescu, ``Cycloaddition Reactions``, Editura Academici, Bucuresti, 1987.
13. G. Surpateanu, P. Decock, N. Avarvari, D. Scutaru, and N. Hurduc, *Iran. Polym. J.*, 1996, **5**, 193 [*Chem. Abstr.*, 1996, **125**, 329625y].
14. N. A. Bailey, S. E. Hull, G. F. Kersting, and J. Morrison, *Chem. Commun.*, 1971, 1429.
15. L. Toupet and Y. Delugeard, *Acta Cryst.*, 1979, **B35**, 1935.
16. C. Bugg, R. Desiderato, and R. L. Sass, *J. Am. Chem. Soc.*, 1964, **86**, 3157.
17. Y. Karzazi, G. Surpateanu, C. N. Lungu, and G. Vergoten, *J. Mol. Struc.*, 1997, **406**, 45.
18. N. A. Bailey and C. G. Newton, *Cryst. Struct. Commun.*, 1980, **9**, 49 [*Chem. Abstr.*, 1980, **92**, 156223k].
19. H. Wittmann, E. Ziegler, K. Peters, E. M. Peters, and H. G. Von Schnering, *Monatsh. Chem.*, 1983, **114**, 1097.

20. R. E. Banks, R. G. Pritchard, and J. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1769.

21. J. Alvarez-Builla, E. Galvez, A. M. Cuadro, F. Florencio, and S. Garcia-Blanco, *J. Heterocycl. Chem.*, 1987, **24**, 917.

22. Y. Karzazi, G. Vergoten, and G. Surpateanu, *Electron. J. Theor. Chem.*, 1997, **2**, 283.

23. E. Fischer, M. Knippel, K. M. Wollin, A. Kalman, and Gy. Argay, *J. Prakt. Chem.*, 1983, **325**, 261.

24. R. Y. Ning, P. B. Madan, J. F. Blount, and R. I. Frye, *J. Org. Chem.*, 1976, **41**, 3406.

25. B. Abarca, R. Ballesteros, F. Mojarrad, M. R. Metni, S. Garcia-Granda, E. Per Carreno, and G. Jones, *Tetrahedron*, 1991, **47**, 5277.

26. Cambridge Crystallographic Database System 1997, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

27. D. Dorohoi, D. Iancu, and G. Surpateanu, *An. Stiint. Univ. Iasi*, 1981, **27**, 59.

28. G. Surpateanu, D. Dorohoi, and I. Zugravescu, *An. Stiint. Univ. Iasi*, 1975, **21**, 89.

29. D. Dorohoi, H. Partenie, A. J. Barnes, W. J. Orville-Thomas, R. Kellner, K. Taga, and B. W. Landvoigt, *J. Mol. Struc.*, 1993, **293**, 129.

30. D. Dorohoi, V. Holban, A. J. Barnes, W. J. Orville-Thomas, R. Kellner, K. Taga, and B. W. Landvoigt, *J. Mol. Struc.*, 1993, **293**, 133.

31. G. Surpateanu and D. Dorohoi, *An. Stiint. Univ. Iasi*, 1977, **23**, 99 [*Chem. Abstr.*, 1977, **91**, 4845f].

32. E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253; E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3261; E. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3267.

33. E. M. Kosower and B. G. Ramsey, *J. Am. Chem. Soc.*, 1959, **81**, 856.

34. W. H. Stafford, *J. Chem. Soc.*, 1952, 580.

35. D. Dorohoi, H. Partenie, L. Chiran, and C. Anton, *J. Chim. Phys.*, 1994, **91**, 419.

36. D. Dorohoi, G. Surpateanu, and C. Mihul, *An. Stiint. Univ. Iasi*, 1974, **20**, 59 [*Chem. Abstr.*, 1974, **86**, 42628s].

37. D. Dorohoi, L. Sitaru, G. Surpateanu, and C. Mihul, *An. Stiint. Univ. Iasi*, 1974, **20**, 147 [*Chem. Abstr.*, 1974, **86**, 105624k].

38. M. Caprosu, I. Druta, I. Fulger, M. Petrovanu, and D. Dorohoi, *Bul. Inst. Politch. Iasi*, 1990, **36**, 51 [*Chem. Abstr.*, 1990, **117**, 191788l].

39. M. Petrovanu, C. Anton, D. Dorohoi, M. Caprosu, and I. Fulger, *Rev. Roum. Chim.*, 1979, **24**, 733.

40. Y. Karzazi, G. Vergoten, and G. Surpateanu, *Electron. J. Theor. Chem.*, 1997, **2**, 1.

41. K. B. Dillon, J. Halfpenny, and A. Marshall, *J. Chem. Soc., Dalton Trans.*, 1985, 1399.

42. A. Allouch and J. Pourcin, *Spectrochimica Acta*, 1993, **49A**, 571.

43. DMol User Guide, version 2. 3. 6. San Diego: Biosym Technologies, 1994.

44. M. Clark, R. D. Cramer III, and N. Van Opdenbosch, *J. Comp. Chem.*, 1989, **10**, 982.

45. Sybyl, Tripos Associates, 1699 South Hanley Road, Suite 303, St. Louis, Missouri 63144.

46. Y. Karzazi, G. Vergoten, and G. Surpateanu, *J. Mol. Struc.*, 1997, **435**, 35.

47. Y. Karzazi, G. Vergoten, and G. Surpateanu, *Electron. J. Theor. Chem.*, 1997, **2**, 273.

48. C. H. Kline Jr and J. Turkevich, *J. Chem. Phys.*, 1944, **12**, 300.

49. L. Coursin, B. J. Fax, and R. C. Lord, *J. Chem. Phys.*, 1953, **21**, 1170.

50. T. Shimanoushi, Tables of Molecular Vibrational Frequencies Consolidated Vol. I, NSRDS-NBS 39, 1972.

51. Y. Karzazi, Ph. D. Thesis, University of Lille 1, France, 1996.

52. Y. Karzazi, Ph. D. Thesis, University of Littoral, France, 1996.

53. R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, 1970, **92**, 3929.

54. D. B. Boyd and R. Hoffmann, *J. Am. Chem. Soc.*, 1971, **93**, 1064.

55. I. Absar and J. R. v. Wazer, *J. Am. Chem. Soc.*, 1972, **94**, 2382.

56. K. Tatsumi, Y. Yoshioka, A. Yamaguchi, and T. Fueno, *Tetrahedron*, 1976, **32**, 1705.

57. F. Bernardi, H. B. Schlegel, M. H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, 1977, **99**, 5633.

58. F. Volatron and O. J. Eisenstein, *J. Am. Chem. Soc.*, 1984, **106**, 6117.

59. V. Kral, Z. Arnold, V. Jehlicka, and O. Exner, *Collect. Czech. Chem. Commun.*, 1980, **45**, 1236.

60. R. Hoffmann and E. L. Belfoure, *J. Am. Chem. Soc.*, 1982, **104**, 2183.

61. J. R. Bews and C. Glidewell, *J. Mol. Struc.*, 1983, **104**, 105.

62. A. Tachibana, M. Koizumi, I. Okazaki, H. Teramae, and T. Yamabe, *Theor. Chim. Acta*, 1987, **71**, 7.

63. G. Surpateanu, *Rev. Roum. Chim.*, 1984, **29**, 877 [*Chem. Abstr.*, 1984, **103**, 177690w].

64. G. Surpateanu, M. Constantinescu, I. Zugravescu, A. Lablache-Combier, and J. P. Catteau, *Bul. Inst. Politeh. Iasi*, 1985, **31**, 77.

65. J. P. Catteau, P. Karafiloglou, A. Lablache-Combier, N. Lethan, and G. Surpateanu, *Tetrahedron*, 1976, **32**, 461.

66. J. W. Cornforth, R. Gigg, and M. S. Tuti, *Aust. J. Chem.*, 1967, **20**, 2479.

67. W. J. Middleton, E. L. Buhle, J. C. Mc Nally, and M. Zanger, *J. Org. Chem.*, 1965, **30**, 2034.

68. H. Nozaki, Z. Morita, and K. Kondo, *Tetrahedron Lett.*, 1966, 2913.

69. A. Hochrainer and F. Wesseley, *Monatsh. Chem.*, 1966, **97**, 1.

70. R. M. Kosover and B. G. Ramsey, *J. Amer. Chem. Soc.*, 1959, **81**, 856.

71. P. A. Chopard, R. J. G. Searle, and F. H. Devit, *J. Org. Chem.*, 1965, **30**, 1015.

72. A. W. Johnson and R. J. Amel, *Tetrahedron Lett.*, 1966, 819.

73. H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, 1966, **22**, 2145.

74. H. König and J. Metzger, *Chem. Ber.*, 1965, **98**, 3733.

75. I. Zugravescu, E. Rucinschi, and G. Surpateanu, *Rev. Roum. Chim.*, 1971, **16**, 1099.

76. I. Zugravescu, E. Rucinschi, and G. Surpateanu, *An. Stiint. Univ. Iasi*, 1970, **16**, 41.

77. G. Surpateanu, A. Lablache-Combier, M. Constantinescu, and J. Marko, *Tetrahedron Lett.*, 1984, **25**, 5751.

78. H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, 1967, **23**, 545.

79. D. J. Cram, Fundamentals of Carbanion Chemistry, Vol. 4, Academic Press,1965.

80. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, Mc. Graw-Hill, New York, QCPE 141, 1970.

81. R. Hoffman, *J. Chem. Phys.*, 1963, **391**, 397.

82. G. Surpateanu, M. Constantinescu, C. Luchian, M.Petrovanu, I. Zugravescu, and A. Lablache-Combier, *Rev. Roum.Chim.*, 1983, **28**, 831 [*Chem. Abstr.*, 1983, **101**, 6205w].

83. J. P. Catteau, A. Lablache-Combier, J. Grimblot, M. Nastasi, and J. Streith, *Tetrahedron*, 1975, **31**, 2909.

84. G. Surpateanu, M. Constantinescu, C. Luchian, M. Petrovanu, I. Zugravescu, and A. Lablache-Combier, *Rev. Roum. Chim.*, 1983, **28**, 933 [*Chem. Abstr.*, 1983, **101**, 6204v].

85. K. N. Houk, J. Sims, R. E. Duke, R. W. Storzier, and J. K. George, *J. Am. Chem. Soc.*, 1973, **95**, 7287.

86. A. Couture, A. Lablache-Combier, and P. Grandclaudon, *Heterocycles*, 1990, **31**, 2111.

87. G. Surpateanu, A. Lablache-Combier, P. Grandclaudon, and B. Mouchel, *Heterocycles*, 1987, **26**, 863.

88. M. Petrovanu, C. Luchian, G. Surpateanu, and V. Barboiu, *Tetrahedron*, 1981, **37**, 2805.

89. M. Petrovanu, C. Luchian, G. Surpateanu, and V. Barboiu, *Tetrahedron*, 1981, **37**, 2813.

90. M. Petrovanu, C. Luchian, G. Surpateanu, and M.Constantinescu, *Tetrahedron*, 1983, **39**, 2417.

91. I. Zugravescu, E. Rucinschi, and G. Surpateanu, *An. Stiint. Univ. Iasi*, 1970, **14**, 41.

92. B. Delley, *J. Chem. Phys.*, 1990, **92**, 508.

93. J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.

94. J. A. Pople, D. L Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

95. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.

96. M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.

97. M. J. S. Dewar, E. G. Zoebish, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

98. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.

99. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.

100. Hyperchem User Manuel, Release 4. 5. Ontario, Hypercube. Inc., 1995.

101. J. J. P. Stewart, *Quant. Chem. Prog. Exch.*, 1990, **10**, 86.

102. C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 1959, **30**, 777.

103. C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 1958, **29**, 864.

104. N. N. Gerasimchuk, A. N. Chernega, and A. A. Kapshuk, *Zh. Neorg. Khim.*, 1993, **233**, 1530.

105. L. Devos, PhD. Thesis, University of Lille1, France, 1982.

106. M. Harel, PhD. Thesis, University of Rehovot, Israel, 1974.

107. R. G. Little, D. Paulter, and P. Coppens, *Acta Cryst.*, 1971, **B 27**, 1493.

108. A. Hoekstra, T. Spoelder, and A. Vos, *Acta Cryst.*, 1972, **B 28**, 14.

109. T. Sundaresan and S. C. Wallwork, *Acta Cryst.*, 1972, **B 28**, 3065.

110. R. R. Lucchese and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1977, **99**, 13.

111. C. A. G. O. Varma and E. J. J. Groenen, *Recl. Trav. Chim.*, 1972, **91**, 296.

112. J. Trotter, *Tetrahedron*, 1960, **8**, 13.

113. R. Destro, C. M. Gramaccioli, and M. Simonetta, *Acta Cryst.*, 1968, **B 24**, 1369.

114. J. A. La Villa and J. L. Goodman, *Tetrahedron Lett.*, 1990, **31**, 6287.

115. M. Petrovanu, G. Surpateanu, and I. Zugravescu, *Mem. Acad. Roum.*, 1984, 2.

116. I. Zugravescu, M. Constantinescu, G. Surpateanu, A. Lablache-Combier, and L. Devos, *Rev. Roum. Chim.*, 1979, **24**, 1089 [*Chem. Abstr.*, 1979, **92**, 93770p].

117. G. Surpateanu, N. C. Lungu, N. Avarvari, A. Lablache-Combier, P. Grandclaudon, and A. Couture, *J. Chem. Phys.*, 1994, **91**, 1648.

118. G. Surpateanu, N. Foca, I. Zugravescu, and E. Rucinshi, *An. Stiint. Univ. Iasi*, 1973, **19**, 31 [*Chem. Abstr.*, 1973, **79**, 142698p].

119. G. Surpateanu, N. Foca, E. Rucinshi, and I. Zugravescu, *An. Stiint. Univ. Iasi*, 1973, **19**, 33.

120. F. Kröhnke and K. Gerlach, *Chem. Ber.*, 1962, **95**, 1108.

121. F. Kröhnke and H. Kubler, *Chem. Ber.*, 1970, **70**, 538.

122. I. Zugravescu, E. Rucinshi, and G. Surpateanu, *Tetrahedron Lett.*, 1970, **12**, 941.

123. M. Petrovanu, I. Druta, and M. V. Tri, *Rev. Roum. Chim.*, 1978, **23**, 781 [*Chem. Abstr.*, 1978, **89**, 128757g].

124. M. Petrovanu, M. V. Tri, and V. Barboiu, *Rev. Roum. Chim.*, 1976, **21**, 717 [*Chem. Abstr.*, 1976, **85**, 63015j].

125. M. Petrovanu, E. Stefânescu, and I. Druta, *Rev. Roum. Chim.*, 1971, **16**, 1107 [*Chem. Abstr.*, 1971, **75**, 98524v].

126. M. Petrovanu, C. Luchian, G. Surpateanu, and V. Barboiu, *Rev. Roum. Chim.*, 1979, **24**, 733 [*Chem.*

Abstr., 1979, **92**, 128299w].

127. G. Surpateanu, M. Constantinescu, and I. Zugravescu, *Rev. Roum. Chim.*, 1978, **23**, 1449 [Chem. *Abstr.*, 1978, **90**, 103198h].
128. G. Klopman, Chemical Reactivity and Reaction Paths, John-Wiley, New York, 1974.
129. G. Klopman, *J. Am. Chem. Soc.*, 1968, **90**, 223.
130. L. Salem, *J. Am. Chem. Soc.*, 1968, **90**, 553.
131. K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, 1973, **95**, 7301.
132. M. Petrovanu, G. Surpateanu, M. Bourceanu, and V. Barboiu, *Tetrahedron*, 1985, **41**, 3673.
133. G. Surpateanu, N. Caea, L. Sufletel, and P. Granclaudon, *Rev. Roum. Chim.*, 1995, **40**, 529 [*Chem. Abstr.*, 1995, **124**, 263360d].
134. A. M. Cuadro, J. L. Novella, A. Molina, J. Alvarez-Builla, and J. Vaquero, *Tetrahedron*, 1990, **46**, 6033.
135. G. Surpateanu, A. Lablache-Combier, P. Granclaudon, A. Couture, and B. Mouchel, *Rev. Roum. Chim.*, 1993, **38**, 671 [*Chem. Abstr.*, 1993, **121**, 157575f].
136. B. Abarca, R. Ballesteros, M. R. Metni, G. Jones, D. J. Ando, and M. B. Hursthouse, *Tetrahedron Lett.*, 1991, **32**, 4977.
137. D. Moderhack and D-O. Bode, *J. Chem. Soc., Perkin. Trans. 1*, 1992, 1483.
138. F. Kröhnke, *Ber.*, 1935, **68**, 1117.
139. C. A. Henrick, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, 1967, **20**, 2441.
140. A. R. Katritzky and D. Moderhack *J. Chem. Soc., Perkin Trans. 1*, 1976, 909.
141. M. F. Aldersly, S. H. Chishti, F. M. Dean, M. E. Douglas, and D. S. Ennis, *J. Chem. Soc., Perkin. Trans. 1*, 1990, 2163.
142. A. Padwa, D. J. Austin, L. Precedo, and L. Zhi, *J. Org. Chem.*, 1993, **58**, 1144.
143. K. Matsumoto, T. Uchida, M. Toda, K. Aoyama, A. Kakehi, A. Shigihara, and J. W. Lown, *Tetrahedron Lett.*, 1992, **33**, 7643.
144. K. Matsumoto, T. Uchida, K. Aoyama, M. Nishikawa, T. Kuroda, and T. Okamoto, *J. Heterocycl. Chem.*, 1988, **25**, 1793.
145. K. Matsumoto, T. Uchida, T. Sugi, and Y. Yagi, *Chem. Lett.*, 1982, 869.
146. U. Bergsträβer, A. Hoffman, and M. Regitz, *Tetrahedron Lett.*, 1992, **33**, 1049.
147. V. Figala, T. Geβner, R. Gomppere, E. Hädicke, and S. Lensky, *Tetrahedron Lett.*, 1993, **34**, 6375.
148. O. Tsuge, S. Kanemasa, K. Sakamoto, and S. Takenaka, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2513.
149. T. Tisher, I. Kadas, Z. Bende, and L. Töke, *J. Heterocycl. Chem.*, 1991, **28**, 867.
150. R. C. F. Jones, and K. J. Howard, *J. Chem. Soc., Perkin. Trans. 1*, 1993, 2391.

151. A. Diaz-Ortiz, E. Diez-Barra, A. de la Hoz, A. Loupy, A. Petit, and L. Sanchez, *Heterocycles*, 1994, **38**, 785.

152. J. Alvarez-Builla, G. Quintanilla, C. Abril, and T. Gandasegui, *J. Chem. Research (S)*, 1984, 202.

153. X. Wei, Y. Hu, T. Li, and H. Hu, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2487.

154. K. Matsumoto, H. Katsura, T. Uchida, K. Aoyama, and T. Machiguci, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2599.

155. K. Matsumoto, and T. Uchida, *Heterocycles*, 1979, **12**, 661.

156. T. Uchida, H. Nishioka, M. Yoshida, and A. Kakehi, *J. Heterocycl. Chem.*, 1995, **32**, 367.

157. T. Uchida, H. Nishioka, M. Yoshida, and A. Kakehi, *J. Heterocycl. Chem.*, 1997, **34**, 203.

158. W. Sliwa, *Heterocycles, 1996*, **43**, *2005.*

159. Y. Matsuda, M. Yamashita, K. Takahashi, S. Iole, K. Furuno, K. Torisu, T. Iton, and C. Motokawa, *Heterocycles*, 1992, **34**, 899.

160. A. M. Cuardo, J. Valenciano, J. J. Vaquero, J. L. Garcia Navio, and J. Alvarez-Builla, *Tetrahedron*, 1993, **49**, 3185.

161. A. Kakehi, S. Ito, and Y. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1769.

162. K. Matsumoto, T. Uchida, and C. Uno, *Heterocycles*, 1982, **19**, 1849.

163. K. Matsumoto, T. Uchida, Y. Ikemi, H. Fujita, K. Aoyama, and M. Asahi, *Heterocycles*, 1986, **24**, 339.

164. W. Stödeli, and W. von Philips born, *Org. Magn. Reson.*, 1981, **15**, 106.

165. H. Fujita, J. Yamauchi, K. Matsumoto, H. Ohya-Nishiguchi, and Y. Deguchi, *J. Magn. Res.*, 1979, **35**, 171.

166. H. Fujita, J. Yamauchi, K. Matsumoto, and H. Ohya-Nishiguchi, *J. Chem. Soc., Perkin Trans. 2*, *1982, 895.*

167. J. A. La Villa, and J. L. Goodman, *Tetrahedron Lett.*, 1990, **31**, 6287.

Received, 13th July, 1998