Ultraviolet Photoelectron, Electron Transmission and *Ab Initio* Study of the Factors Determining the Stability of Imines

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The electronic structure of several alkyl-, *N*-bis(trimethylsilyl)methyl- (BTMSM), and *C*-phenyl-substituted imines **1**–**11** have been determined by *ab initio* 3-21G* calculations. The calculations reproduce with good accuracy the available geometry of methylenimine, **1**, obtained by microwave spectroscopy[1] and *ab initio* 6-31G** calculations[2] as well as the outermost energy levels experimentally determined by ultraviolet photoelectron spectroscopy for several derivatives. The analysis of the results of the calculations indicate that alkyl substitution of **1** at the nitrogen atom reduces the charge separation at the double bond increasing stabilisation, while substitution at the carbon atom has the opposite effect. Steric hindrance of the substituent(s) and the energy gaps between filled (nitrogen lone pair, HOMO and π_{CN}) and virtual (π^*_{CN}) orbitals play a secondary role on stability.

All the BTMSM and phenyl derivatives studied are stable in air at room temperature irrespective of other substituents present. Our analysis indicates that these substituents change the energy, ordering and localisation properties of the valence MOs. In particular, the nitrogen lone pair orbital is no longer the HOMO.

The imines of carbonyl derivatives have been extensively investigated due to their importance as synthons[3] as, for example, in the Staudinger reaction leading to the formation of the β-lactam skeleton present in various families of antibiotics.[4,5]

The geometric and electronic structures of the parent imine, CH_2=NH, have been determined by microwave spectroscopy,[1] ultraviolet photoelectron spectroscopy (UPS),[6] and *ab initio* calculations.[1,7–12] Similarly, UPS spectra and semiempirical calculations are available for several imines bearing small alkyl substituents.[13–19] These compounds are unstable and dimerise or polymerise easily (unless stored under nitrogen and at low temperature).[14–21] Generally, their physical properties have been obtained on freshly prepared samples or samples generated *in situ*. Often, *N*-methylene amines are more stable when the nitrogen atom is attached to a tertiary carbon[22] than when the carbon bearing the nitrogen has a lower degree of substitution.[23,24] Recently, it has been reported[25] that the presence of a bis(trimethylsilyl)methyl [$-HC(SiMe_3)_2$, BTMSM] substituent on nitrogen stabilises otherwise unstable Schiff bases.

The aim of the present work is to investigate the electronic structure of imines bearing different types of substituents to elucidate the factors which determine their stability in terms of the Frontier Orbital Model. In particular, we have analysed the UPS and Electron Transmission (ET) spectra of selected alkyl-, BTMSM- and phenyl-imines and performed *ab initio* 3-21G* calculations on them and related derivatives in order to reproduce the experimental spectroscopic valence orbital energies, and to determine their geometry and the distribution of the electronic charge density on the various atoms and groups.

The compounds studied, of general formula HR^1C=NR^2, are listed below, where S and U indicate stable and unstable compounds, respectively, in air at room temperature. (The stability of compounds **2** and **6** is predicted, see below.)

	R^1	R^2			R^1	R^2	
1	H	H	U	**7**	H	BTMSM	S
2	Bu^t	H	(U)	**8**	Me	BTMSM	S
3	Bu^t	Bu^t	U	**9**	Bu^t	BTMSM	S
4	H	Bu^t	S	**10**	Ph	BTMSM	S
5	Me	Bu^s	U	**11**	Ph	Me	S
6	H	Bu^s	(S)	**12**	$H_2C(SiMe_3)_2$		

The UPS spectra were obtained for **4**, **7** and **10**, while those of **1**,[6] **11**[13,18] and **12**[26,27] were available from the literature. The calculations were also carried out on bistrimethylsilylmethane [$H_2C(TMS)_2$, **12**] for comparison and assignment purposes. ET spectra were also recorded for compounds **4** and **7**.

Experimental

Ultraviolet Photoelectron Spectroscopy.—The UPS spectra were obtained with a Perkin-Elmer PS 18 photoelectron spectrometer connected to a Datalab DL4000 signal analysis system. The bands, calibrated against rare-gas lines, were located using the positions of their maxima, which were taken as corresponding to the vertical ionisation energies (E_is). The accuracy of the E_i values was estimated to be better than ± 0.05 eV (except for shoulders).

Electron Transmission Spectroscopy.—ETS allows determination of the energy (Attachment Energy, AE) at which electrons are temporarily captured by an atomic or molecular species in the gaseous phase. These AE values are, to a first approximation, the negative of the vertical electron affinities of the capturing species. The electron transmission experiment has been previously described.[28] Our apparatus[29] is in the format devised by Sanche and Schulz.[30] The derivative of the transmitted current as a function of the incident electron energy is recorded. ET spectra were obtained using the apparatus in the 'high-rejection' mode (except where specified), which yields a

Table 1 Geometry,[a] energy levels (eV), and C–N charge separation (Δq, e$^-$) of $H_2C{=}NH$ (C_s)

	6-31G**[b]	Microwave[c]	3-21G
$C-H_1$	1.090	1.09	1.081
$C-H_2$	1.086	1.09	1.075
C–N	1.250	1.273	1.256
$N-H_3$	1.011	1.021	1.015
H_1-C-N	124.7	125.1	125.31
H_2-C-N	119.3	117.9	119.26
$C-N-H_3$	110.0	110.4	114.93
Δq_{C-N}	0.43		0.475
N_{lp}	−11.5		−11.08 (10.60)[d]
π_{C-N}	−12.3		−12.19 (12.50)[d]

[a] Bond lengths in Å, bond angles in degrees. [b] From ref. 2. [c] From ref. 1. [d] Experimental E_i values from ref. 6.

signal related to the nearly total electron scattering cross-section.[31] The attachment energies reported correspond to the vertical midpoints between the minima and maxima of the differentiated signal. The energy scales were calibrated by using the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV according to the number of decimal places reported.

The compounds studied were prepared according to literature methods.[22,25]

Results

Ab initio 3-21G Calculations of the Geometry of the Imines.*—Table 1 shows a comparison of the calculated geometry for the imine **1** in the planar (C_s) conformation, with values obtained by microwave analysis[1] and 6-31G** calculations.[2] The Table also includes the calculated energies of the two uppermost occupied MOs (the nitrogen lone pair, N_{lp}, the $\pi_{C=N}$ MO), the corresponding experimental E_i values[6] and the calculated difference between the total charge at the carbon and nitrogen atoms [$\Delta q_{(C=N)}$]. The present calculations reproduce quite well the experimental data and the results of the more sophisticated calculations, making us confident regarding their use for the larger derivatives analysed, for which the 6-31G** calculations are impracticable. The 3-21G* calculations, therefore, appear to be a satisfactory compromise between accuracy and required computer time.

The geometry was completely optimised for all the compounds. It turns out that: (i) when two substituents are present, the *E*-conformer is the more stable [by 11.95 (**5**), 8.77 (**8**), 40.35 (**9**), 28.98 (**10**), 27.6 (**11**) kJ mol^{-1}; (ii) the C–N bond distance is scarcely dependent on the nature and number of the substituents (d_{CN} = 1.254 ± 0.002 Å, except for **10** where it is 1.261 Å); (iii) in **10** and **11**, the phenyl ring lies in the C–N–H plane; (iv) one of the three $C-C_3$ or $C-H_3$ bonds of the substituent lies in the main plain of the imine group, *syn* to the double bond; (v) in the derivatives bearing the CHR_2 groups (R = alkyl or trimethylsilyl), the C–H bond is *syn* to the C=N double bond.

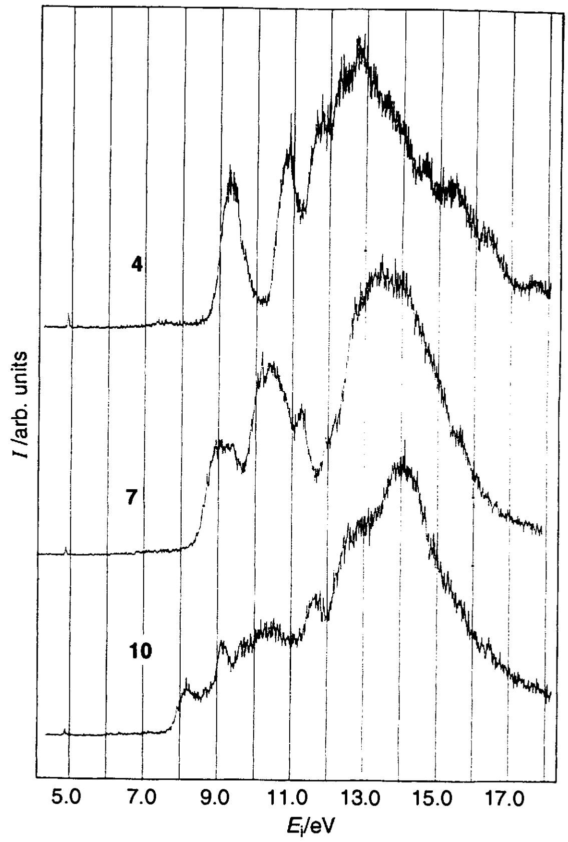

Fig. 1 He I photoelectron spectra of compounds **4**, **7** and **10**

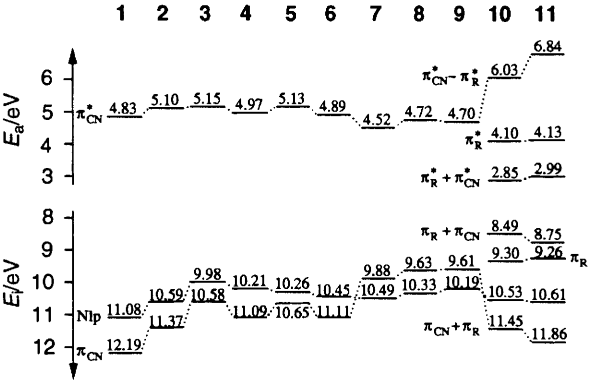

Fig. 2 *Ab initio* 3-21G* partial energy level diagrams for imines **1–11**

Assignment of the UPS and ET Spectra.—The UPS spectra of compounds **4**, **7** and **10** are shown in Fig. 1. The E_i values obtained from the spectra are listed in Table 2 together with those of compounds **1**,[6,14] **11**[18] and **12**[26,27] which are used for the assignment and discussion. E_i1 and E_i2 of **1** have been assigned[6] to ionisation from the N_{lp} and π_{CN} MO, respectively. The substitution of a Bu^t group for the hydrogen atom bonded to the nitrogen leads in **4** to a large destabilisation of both energy levels (1.35 and 1.7 eV, respectively). These shifts are in line with those reported[14a] for *N*-methylation (0.7 and 0.8 eV). Further ionisations, between 11.70 and 12.3 eV, are assigned to electron extraction from the MOs mainly localised at the C–C bonds of the substituent. These bands are stabilised with respect to the corresponding ones in Bu^t-ethene (2,2′-dimethylbut-3-ene: 11.2, 11.6 and 12.0 eV[32]) because of the high electronegativity of the nitrogen atom and the symmetry-allowed mixing not only with the double bond but also with the N_{lp} orbital. The computations confirm the N_{lp} above π_{CN} ordering as shown in Fig. 2.

Compound **7** can be considered to derive from **4** by substitution of the BTMSM group for the *tert*-butyl group. An estimation of the E_i values of the BTMSM group before interaction with the orbitals of the C=N fragment can be obtained from the corresponding data of compound **12**. The upper part of the UPS spectrum of **12** shows[27] a broad intense band centred at 10.4 eV flanked by two sharp, less intense bands at 9.5 and 11.4 eV. These features have been assigned[26] to six ionisation events from the C–Si bonds: the first and the last one mainly derive from the anti-bonding and bonding interaction, respectively, of the p_x orbitals of the heavy atoms lying along the C–Si–C–Si–C axis, and the central band to ionisation from four

Table 2 Valence ionisation energy values (eV) of Schiff bases with assignments (in parentheses)

		E_i1	E_i2	E_i3	E_i4
1	H_2CNH[a]	10.60 (N_{lp})	12.50 (π_{CN})		
4	H_2CN–Bu^t	9.25 (N_{lp})	10.8 (π_{CN})	11.70 (σ_{CC})	12.30 (π_{CC})
12	$H_2C(TMS)_2$[b]	9.5 (σ_{Si-C})	10.4 (σ_{Si-C} and π_{Si-C})	11.4 (σ_{Si-C})	
7	H_2CN–BTMSM	9.0 ($\pi_{CN} + \sigma_{Si-C}$)	9.4 (N_{lp})	10.4 (σ_{Si-C} and π_{Si-C})	11.2 (σ_{Si-C})
11	HPhCN–Me[c]	8.77 ($\pi_R + \pi_{CN}$)	9.38 (π_R)	9.6 (N_{lp})	10.87 (π_{CN})
10	HPhCN–BTMSM	8.2 ($\pi_R + \pi_{CN} + \sigma_{Si-C}$)	9.15 (π_R)	9.7 (N_{lp})	10.35 (σ_{Si-C} and π_{Si-C})

[a] From ref. 14a. [b] From ref. 26. [c] From ref. 18.

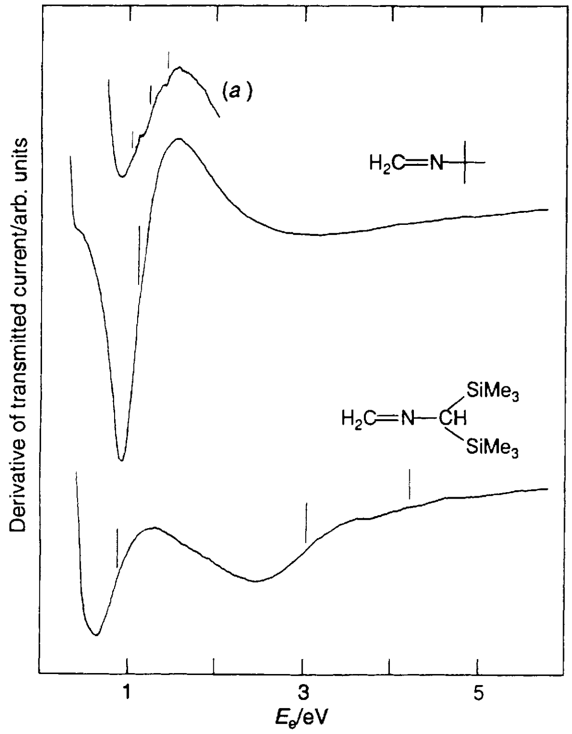

Fig. 3 Derivative of the electron current transmitted through compounds **4** and **7** as a function of electron energy. (*a*) Recorded in the 'low-rejection' mode.

orbitals mainly deriving from their p_z and p_y (π) AOs. The corresponding 3-21G* values, fully support this assignment.

In the most stable conformation of compound **7** the HOMO of the BTMSM fragment interacts with the π_{CN} MO. The resulting anti-bonding combination produces one of the two components of the first band with partially resolved maxima at 9.0 and 9.4 eV. The band of the corresponding bonding combination is assigned below. The broad intense band centred at 10.4 eV is due to electron extraction from the remaining C–Si p orbitals. The N_{lp} orbital in **7** is expected to be slightly stabilised with respect to the corresponding orbital in **4** (9.25 eV) because the interaction of the lone pair and the in-plane C–C orbital of the *tert*-butyl group is substituted in **7** by the interaction with the lower-lying C–H orbital. We can, therefore, assign the maxima at 9.0 and 9.4 eV of the first band in the spectrum of **7** to the π_{CN}/σ_{C-C_3} and N_{lp} orbitals, respectively. This assignment is supported by the results of the calculations (see Fig. 2) and bears evidence of the inversion of the two uppermost occupied orbitals in **7** with respect to the alkyl-substituted imines hitherto reported.[6,13–19] The good correlation between experimental E_i values and computed energy levels indicates that the bonding combination of the HOMO of the BTMSM fragment and the π_{CN} orbital gives rise to the band at 12.1 eV in the spectrum of **7**. In addition, the calculations indicate that the LUMO in **7** (π^*_{CN} 4.52 eV) is stabilised with respect to the corresponding orbital in **4** by 0.45 eV (see Fig. 2). The stabilisation arises from interaction with the σ^*_{Si-C} MOs, essentially localised at the Si atoms. This interaction decreases the localisation of the LUMO at the C atom. These results are fully consistent with the ET spectra of **4** and **7**, reported in Fig. 3. The ET spectrum of **4** displays a single sharp resonance at 1.11 eV, associated with electron capture into the π^*_{CN} orbital. In the 'low-rejection' spectrum (related to the differential backscattering cross-section[31]) a vibrational progression with spacing of about 220 meV is also present. The π^*_{CN} resonance in **7** lies at 0.89 eV. In addition, low energy resonances (3.01, 4.3 eV) are present, which are due to electron capture into σ^*_{Si-C} MOs.[14]

Compound **10**, HPhC=N–BTMSM, can be considered to derive from **11**, HPhC=N–Me, by substitution of a BTMSM group for the methyl group. The assignment of the four outermost ionisation energy values of **11**, obtained on experimental basis,[18] is reported in Table 2. Fig. 2 shows that it is fully confirmed by the present calculations which provide, in addition, the following ordering of the three lowest-lying empty MOs: $\pi^*_R + \pi^*_{CN} = 2.99$, $\pi^*_R = 4.13$, $\pi^*_{CN} - \pi^*_R$ 6.48 eV. In this molecule, therefore, the HOMO and the LUMO are delocalised at the phenyl ring and the CN group, the second HOMO and the second LUMO are localised only on the ring. The MOs with large π_{CN} and π^*_{CN} character are significantly stabilised and destabilised, respectively, with respect to the corresponding orbitals of alkylimines.

The poor quality of the UPS spectrum of **10** does not allow a detailed assignment. However, we expect, by analogy with the spectrum of **7**, that the mixing with the orbitals of the BTMSM group will destabilise the HOMO and stabilise the π^*_{CN} MO with respect to **11**. In addition, we expect that the second and the third filled and the second empty MOs will be only slightly affected by substitution because they are highly localised at the ring or the N lone pair, and that the filled orbitals mainly localised at the BTMSM group will be responsible for the ionisations between about 10 and 11 eV. These expectations are verified in the spectrum (see Table 2), and confirmed by calculations (see Fig. 2) although for **10** a detailed analysis of the eigenvectors, except for the first few, is difficult because of the extensive delocalisation of the MOs over this relatively large molecule with low symmetry.

We see, therefore, that the present *ab-initio* 3-21G* calculations for these imines reproduce with good accuracy the energy trends and localisation properties of the MOs determined experimentally and the geometry and electron charge distribution obtained from more sophisticated calculations for **1**. They can, therefore, be used with confidence to obtain the energy level values of related imines and their charge distribution.

Table 3 lists the electron charges at the various atoms or groups, the charge difference between the carbon and the nitrogen atoms of the double bond, the energy difference between the LUMO and the N_{lp} and π_{CN} orbitals for the imines **1**–**11** computed at the 3-21G* level.

Table 3 Charge (e) at various atoms or groups and energy difference (eV) between the LUMO, π^*_{CN}, and the π_{CN} or N_{lp} orbitals for imines **1**–**11**, $HR^1C{=}NR^2$, obtained by *ab initio* 3-21G* calculations

Compound[b]											
	R^1	R^2	q_H	q_{R^1}	q_{R^2}	q_C	q_N	Δq_{C-N}	$\Delta\pi^*/N_{lp}$	$\Delta\pi^*/\pi$	Stability[a]
1	H	H	0.183	0.216	0.292	−0.110	−0.585	0.475	15.91	17.02	U
2	Bu^t	H	0.195	−0.070	0.285	0.225	−0.635	0.860	15.69	16.47	(U)
3	Bu^t	Bu^t	0.201	−0.084	0.206	0.255	−0.578	0.833	15.13	15.73	U
4	H	Bu^t	0.184	0.212	0.217	−0.101	−0.512	0.411	15.18	16.90	S
5	Me	Bu^s	0.189	0.013	0.207	0.130	−0.539	0.669	15.39	15.79	U
6	H	Bu^s	0.175	0.212	0.221	−0.103	−0.505	0.402	15.34	16.00	(S)
7	H	BTMSM	0.177	0.212	0.252	−0.106	−0.535	0.429	15.01	14.40	S
8	Me	BTMSM	0.192	0.013	0.236	0.129	−0.570	0.699	15.05	14.35	S
9	Bu^t	BTMSM	0.191	−0.084	0.234	0.254	−0.595	0.849	14.89	14.31	S
10	Ph	BTMSM	0.234	−0.087	0.264	0.165	−0.575	0.740	16.56	17.48	S
11	Ph	Me	0.207	−0.064	0.233	0.225	−0.601	0.826	17.45	18.70	S

[a] U = unstable, S = stable in air at room temperature; (S) and (U): predicted stability, see text. [b] R^1 and R^2 are the substituents located at the carbon and nitrogen atom of the double bond, respectively.

Discussion

We begin our analysis from the alkyl derivatives **2**–**6**. Compound **4**, which bears a substituent at the N atom, is stable, while compounds **3** and **5**, which also have a substituent at the C atom, have been reported to be very unstable.[25] From the data shown in Table 3 it is possible to observe that the alkyl group decreases significantly the electron charge density at the carbon atom to which it is bonded, while increasing electron density at the nitrogen atom. This outcome results from the higher electronegativity of the central carbon atom of the alkyl group with respect to hydrogen, and from the polarisation of the double bond towards the nitrogen atom deriving[29,33] from the mixing of the π and π* orbitals of the C=N group with the pseudo π and π* orbitals of the substituent. The effect of the alkyl group at carbon is therefore to increase the charge separation between the atoms of the double bond from 0.411 (**4**) to 0.699 (**5**) and 0.833 (**3**) electrons, favouring di(poly)-merisation.

Another factor which could play a role in this reaction is the energy difference between the frontier orbitals, namely $\Delta(\pi^*_{CN} - N_{lp})$ and $\Delta(\pi^*_{CN} - \pi_{CN})$. Although we do not know which is the donor orbital involved in the attack leading to polymerisation,† it is possible to observe that $\Delta(\pi^*_{CN} - N_{lp})$ and the localisation of these MOs do not change significantly on going from **3** to **5**. On the other hand, if the first act of the reaction involves the π_{CN} MO, the higher stability of **4** could be related to the larger $\Delta(\pi^*_{CN} - \pi_{CN})$ value with respect to the other alkyl derivatives (see, however, the discussion on silyl and phenyl derivatives).

The steric hindrance due to the substituents also has to be considered. For example, although both Δ values are the largest for **1** which also has a small Δq, the compound is unstable. It turns out that both **1**, where steric hindrance is nearly absent, and **3**, where it is greatest, are both unstable. Thus, although both steric hindrance and energy separation between filled and empty MOs certainly play a role in determining the stability of alkyl imines, the Δq value seems to be the most important single factor (except for **1**, where the low steric hindrance appears to dominate).

To our knowledge, compounds **2** and **6** have not been hitherto synthesised. On the basis of the above reasoning, it is possible to predict that **2** should be unstable because the substitution results, with respect to **1** or **4**, in a very large increase of Δq, while the energy differences between empty and filled orbitals do not change significantly. On the other hand, **6** should be stable because the substitution of the methyl group with a hydrogen atom decreases Δq with respect to **5**. This prediction is in agreement with the stability observed for *N*-cyclohexylimine, $H_2C{=}N{-}C_6H_{11}$.[34]

We turn now to the silicon derivatives **7**–**9**. In comparing the pairs **7**–**4**, **8**–**5** and **9**–**3**, which have similar steric hindrance, we observe (see Table 3) that the electron charge distribution within each pair is nearly equal when a small charge shift (0.01–0.02 e) from the BTMSM group towards the nitrogen atom is taken into account. In particular, Δq increases with the size of the substituent from 0.429 e (**7**) to 0.699 e (**8**) and 0.849 e (**9**) in agreement with the increase of the polarising effect of the *C*-substituent, and parallels the trend observed for the alkyl derivatives: 0.411 e (**4**), 0.669 e (**5**) and 0.833 e (**3**). In addition, the energy gaps between the LUMO and the two uppermost occupied MOs are smaller in the silicon derivatives favouring intermolecular reactions. But, at variance with the alkyl derivatives, all the silyl derivatives are stable. It appears that for the BTMSM derivatives there is present an additional factor which overwhelms all the others. What does change in the silyl derivatives is the nature of both the frontier orbitals. In fact, as previously discussed for **7**, the mixing with the uppermost filled orbital of the BTMSM group pushes the π_{CN} orbital above the N_{lp} orbital also in **8** and **9**. At the same time, the LUMO is lowered by strong mixing with the relevant σ^*_{Si-C} orbital of the substituent but its localisation at the carbon atom decreases. The lack of reactivity of compounds **8** and especially **9** which has the smallest $\Delta(\pi^*_{CN} - \pi_{CN})$ value and one of the highest Δq strongly suggests that dimerisation starts by interaction of the N_{lp} orbital with the π^*_{CN} and that this interaction is inhibited in the BTMSM derivatives, where the N_{lp} is not the HOMO, probably by a screening effect of the outer π_{CN} MO and by the reduced coefficient at the carbon atom of the π^*_{CN} orbital. This conclusion is supported by the stability of compounds **10** and **11** where the two uppermost filled and the two lowermost empty MOs are largely or exclusively localised at the phenyl ring.

Conclusions.—To investigate the origin of the different stability of alkyl imines varying the size and the position of the substituent(s) and the stability imparted to imines by silyl and phenyl substituents, we have determined by *ab initio* 3-21G* computations the energy and localisation properties of the valence MOs and the charge distribution of compounds **1**–**12**. We have first demonstrated that our calculations reproduce with good accuracy the experimental assignment of the UPS spectra of compounds **1**, **4**, **7** and **10**–**12** as well as the C–N charge separation of **1** obtained by 6-31G** computations[2] and the geometric parameters obtained by the same calculations and microwave spectroscopy.[1]

It turns out that the stability of alkyl derivatives depends on

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† To clarify this problem, *ab initio* calculations on simple imines are currently underway in our laboratories.

the interplay of steric hindrance of the substituents, the energy separation between filled and empty frontier orbitals, and mainly from the electron charge separation between the atoms of the double bond, Δq. It has been observed, also, that Δq decreases by alkyl substitution at nitrogen, while it increases by substitution at carbon favouring stability and instability, respectively.

In the silyl derivatives the most prominent factor is the symmetry-allowed mixing of the orbitals of the substituent with the π_{CN} and π^*_{CN} orbitals. The result of these interactions is a strong destabilisation of π_{CN} which becomes the HOMO and a sizeable localisation of π^*_{CN} also at the substituent. In the phenyl derivatives, the two uppermost filled π-ring orbitals lie above π_{CN} and the two lowest vacant orbitals have large ring character. In both cases the N_{lp} orbital is no longer the HOMO. The general stability imparted to imines by these substituents strongly suggests that the attack leading to di(poly)merisation involves the N_{lp} and the π^*_{CN} orbitals.

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