The Journal of Physical Chemistry A

VOLUME 102, NUMBER 48, NOVEMBER 26, 1998

LETTERS

Effect of Silyl Substitution on the Frontier Orbitals of Diimines

Alberto Modelli* and Francesco Scagnolari

Università di Bologna, Dipartimento di Chimica "G. Ciamician", via Selmi 2, 40126 Bologna, Italy

Derek Jones

Consiglio Nazionale delle Ricerche, Istituto ICoCEA, via Gobetti 101, 40129 Bologna, Italy

Giuseppe Distefano

Università di Ferrara, Dipartimento di Chimica, via Borsari 46, 44100 Ferrara, Italy

Received: August 13, 1998; In Final Form: September 29, 1998

Temporary anion formation in diimines bearing CH_3, $C(CH_3)_3$, and $Si(CH_3)_3$ substituents is studied by means of electron transmission spectroscopy and ab initio calculations. The sizable reduction in the HOMO−LUMO transition energy caused by silyl substitution is found to be due not only to destabilization of the HOMO, as known from literature data, but also to stabilization of the LUMO, the mainly $\pi^*_{N=N}$ empty orbital.

Introduction

Over the past decade, silicon-containing saturated molecular systems have attracted great attention owing to their interesting mechanical and electronic properties. In particular, oligosilanes absorb in the UV region at sizeably lower energy with respect to the corresponding alkanes, their behavior in this regard resembling more that of unsaturated hydrocarbons. Moreover, it had been previously noted that replacement of an alkyl group adjacent to a chromophoric double bond with a trimethylsilyl group causes a sizable bathochromic shift (see ref 1 and refs therein). This effect is particularly remarkable in bis(*tert*-butyl)diimine, where the color turns to red and then blue upon stepwise substitution of the two *tert*-butyl groups with isoelectronic trimethylsilyl groups. The HOMO−LUMO transition energy is, in fact, reduced by about 1.8 eV in the disubstituted derivative. A study[1] of the trans conformers of these molecules by means of photoelectron spectroscopy and CNDO calculations has demonstrated that each silyl substitution causes a destabilization of about 0.5 eV of the HOMO (n_{N^+}), the symmetric combination of the nitrogen lone pairs of the azo group, in agreement with the calculated negative charge density increase at the nitrogen atoms. Electron donation from the silyl substituents would thus constitute the main factor responsible for the peculiar electronic spectrum, while the possibility of increased electron-acceptor properties, that is, stabilization of the LUMO (π^*), was not considered. Experimental measurement of such a phenomenon is now possible using electron transmission spectroscopy (ETS), which is one of the most suitable means for measuring electron attachment energy (AE) values (that is, the negative of the vertical electron affinity, EA, values) in gaseous samples. This technique takes advantage of the sharp variations in the total electron−molecule scattering cross section caused by resonance processes, namely, temporary capture of electrons with appropriate energy and angular momentum into empty orbitals. We have systematically used ETS for studying the electron-acceptor properties conferred to hydrocarbons by group 14, 15, 16, and 17 elements.[2] The spectra of saturated[3,4] and unsaturated[5,6] trimethylsilyl deriva-

10.1021/jp983378g CCC: $15.00

tives show that $\sigma^*_{\mathrm{Si-C}}$ empty orbitals lie at lower energy with respect to the corresponding $\sigma^*_{\mathrm{C-C}}$ orbitals. Mixing with $\sigma^*_{\mathrm{Si-C}}$ orbitals causes a significant stabilization of the π^* LUMO of ethene, benzene,[5] furan, and thiophene.[6] In the present Letter we extend the ETS analysis, supported by ab initio HF/6-31G** and higher level calculations, to the above cited azo compounds in order to clarify whether the large reduction in the $n_{\mathrm{N^+}} \rightarrow \pi^*$ transition energy caused by silyl substitution can be traced back only to its electron-donating effects or also to an increase in the electron-acceptor properties of the $\pi^*_{\mathrm{N=N}}$ empty orbital.

Experiment and Calculations

Our electron transmission apparatus is in the format devised by Sanche and Schulz[7] and has been previously described.[5] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. The spectra were obtained in the "high-rejection" mode[8] and are therefore related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scales were calibrated with reference to the $(1s^1 2s^2)$ ^2S anion state of He. The estimated accuracy is ±0.05 or ±0.1 eV, depending on the number of decimal digits reported.

Bis(methyl)diimine (**1**), bis(*tert*-butyl)diimine (**2**), and 1-trimethylsilyl-2-*tert*-butyldiimine (**3**) were prepared according to literature procedures.[9,10]

Calculations. The ground- and anion-state geometric parameters for the trans azoderivatives $R_3MN{=}NMR_3$ (MR_3 = CH_3 (**1**), $C(CH_3)_3$ (**2**), and $Si(CH_3)_3$ (**4**)) have been optimized at the HF/6-31G** level using the Gaussian 94 series of programs.[11] To investigate the effect of the inclusion of diffuse functions and of electron correlation energy on the geometry of the negative species, HF/6-31+G* and (only for **1**) MP2 (6-31G**) calculations have been also carried out. The vertical (AE_v) and adiabatic (AE_a) attachment energy values have been obtained with the ΔSCF procedure at the HF/6-31G** (**1**, **2**, and **4**) and HF/6-31+G* (**1** and **2**) levels from the total energy differences between the anion and neutral species by optimizing the anion geometry (AE_a) or at the neutral-state geometry (AE_v).

Results and Discussion

TABLE 1: Experimental and Theoretical Values of Selected Bond Distances (Å), of the M−N═N Bond Angle (deg) and of the N−N−M−R (Φ) Dihedral Angle (deg) for the Trans Conformer of Bis(methyl)-, Bis(*tert*-butyl)-, and Bis(trimethylsilyl)Diimine, $R_3M{-}N{=}N{-}MR_3$, and for the Corresponding Anions[h]

MR_3	$d_{\mathrm{M-N}}$	$d_{\mathrm{N=N}}$	$d_{\mathrm{M-R}}$	M−N═N	Φ
CH_3 (**1**)					
ED[a]	1.482(2)	1.247(3)	1.105(3)	112.3(3)	
ED[b]	1.474(3)	1.254(3)	1.107(6)	111.9(5)	
HF/6-31G**					
neutral	1.454	1.212	1.084−1.085	113.72	0.0
anion	1.440	1.344	1.092−1.101	109.24	0.0
HF/6-31+G*					
neutral	1.453	1.210	1.083−1.084	114.20	0.0
anion	1.441	1.337	1.092−1.097	110.37	0.0
MP2(6-31G**)					
neutral	1.466	1.263	1.089−1.090	111.23	0.0
anion	1.449	1.385	1.099−1.106	107.15	0.0
$C(CH_3)_3$ (**2**)					
X-ray[c]	1.493	1.222	1.537[d]		
HF/6-31G**					
neutral	1.477	1.209	1.528−1.533	116.13	0.0
anion	1.454	1.332	1.538−1.540	110.53	56.2
HF/6-31+G*					
neutral	1.477	1.207	1.528−1.533	116.45	0.0
anion	1.455	1.328	1.538−1.541	111.53	55.6
$Si(CH_3)_3$ (**4**)					
X-ray[e]	1.808	1.171	1.850−1.855	120.0	19.0
ED			1.875[f]−1.887[g]		
HF/6-31G**					
neutral	1.809	1.231	1.880−1.884	116.91	0.1
anion	1.715	1.364	1.907−1.908	109.49	57.6
HF/6-31+G*					
neutral	1.812	1.229	1.881−1.884	117.52	0.1
anion	1.720	1.357	1.908	111.09	57.28

[a] From ref 12. [b] From ref 13. [c] From ref 14. [d] From ref 15. [e] From ref 16. [f] From ref 15. [g] From ref 17. [h] When two $d_{\mathrm{M-R}}$ values are reported, the lowest is related to the M−R bond that lies in the M−N═N plane.

TABLE 2: Computed Bond Distance (Å) and Bond Angle (deg) Variations between the Neutral and the Anion States for Trans Diimines $R_3M{-}N{=}N{-}MR_3$[a]

MR_3	$\Delta d_{\mathrm{M-N}}$	$\Delta d_{\mathrm{N-N}}$	ΔM−N═N
CH_3 (**1**)			
HF/6-31G**	−0.014	0.132	−4.48
HF/6-31+G*	−0.012	0.127	−3.83
MP2/6-31G**	−0.017	0.122	−4.08
$C(CH_3)_3$ (**2**)			
HF/6-31G**	−0.023	0.123	−5.60
HF/6-31+G*	−0.022	0.121	−4.92
$Si(CH_3)_3$ (**4**)			
HF/6-31G**	−0.094	0.133	−7.42
HF/6-31+G*	−0.092	0.128	−6.43

[a] A negative value indicates that the geometric parameter decreases in the anion with respect to the neutral compound.

Table 1 compares the M−N, N═N, and $M{-}R_3$ bond distances and the M−N═N bond angles computed at the HF/6-31G**, HF/6-31+G* (**1**, **2**, and **4**), and MP2/6-31G** (**1**) levels for the ground and ionic states of trans diimines $R_3M{-}N{=}N{-}MR_3$ (MR_3= CH_3, $C(CH_3)_3$, and $Si(CH_3)_3$) with available experimental data. The three levels of calculations reproduce fairly well the experimental geometric parameters and their variation with substitution. The largest discrepancy is with respect to the length of the N═N double bond in **4** for which the computed value is significantly longer (0.06 Å) than that deduced from X-ray diffraction data. The latter value (1.171 Å), however, is not in line with the average experimental value (1.222 Å)[15] and is outside the reported range (1.219-1.254 Å)[13] for trans diimines. On the other hand, the computed bond distance is close to the remaining computed and experimental data (see Table 1). We therefore conclude that on going from the methyl to the *tert*-butyl and trimethylsilyl derivatives the M−N═N bond angle and the N═N bond distance slightly increase. The best agreement between experimental and computed data occurs for **1** for which reliable gas-phase electron diffraction (ED) data and the results of MP2 calculations are compared. In all the cases, the M−N═N−M skeleton is planar, and one of the H (**1**) or C (**2** and **4**) atoms of the substituent lies in the main molecular plane (the dihedral angle ϕ = N−N−M−R = 0°, see Table 1).

Table 2 summarizes the variation of the M−N and N═N bond distances and of the M−N−N bond angles on going from the neutral to the corresponding anion species. A negative value indicates that the geometric parameter decreases in the anion with respect to the neutral compound. The different levels of calculations provide equivalent results. In particular, the double bond lengthens in the anions by 0.12−0.13 Å in accordance with the N−N antibonding character of the singly occupied MO

TABLE 3: Experimental Vertical and Computed Vertical (AE_v) and Adiabatic (AE_a) $\pi^*_{N=N}$ Attachment Energy Values (eV) for Trans Diimines $R_3M-N=N-M'R_3$

MR_3, $M'R_3$	AE_v[a]	AE_a[b]
CH_3, CH_3 (**1**)		
ETS	0.83	
HF/6-31G**	2.69	2.01
HF/6-31+G*	2.12	1.53
$C(CH_3)_3$, $C(CH_3)_3$ (**2**)		
ETS	0.63	
HF/6-31G**	2.45	1.59
HF/6-31+G*	2.08	1.26
$C(CH_3)_3$, $Si(CH_3)_3$ (**3**)		
ETS	≤0.3	
$Si(CH_3)_3$, $Si(CH_3)_3$ (**4**)		
HF/6-31G**	1.64	0.51
HF/6-31+G*	1.27	0.33

[a] The calculated AE_v is the difference between the anion energy at the neutral-state geometry and the neutral-state energy (ΔSCF). [b] AE_a is the calculated energy difference between the geometry optimized anion and the neutral state.

(SOMO), while the M−N bond distance is reduced only slightly (about 0.015 Å) in the alkyl derivatives and more significantly (0.09 Å) in the silyl derivative. In agreement, the calculated localization properties predict the participation of the carbon atoms to the SOMO of **1** and **2** to be very small, while the SOMO of **4** is predicted to possess a sizable Si−N (bonding) character.

It was pointed out in the literature[18,19] that the use of diffuse functions in the 6-31+G* basis set leads to a complete breakdown in the correlation of experimental (first) AEs and LUMO eigenvalues. The inadequacy of diffuse functions for reproducing AE trends from the difference between the total energies of the anion and neutral states was also pointed out.[19] It is to be noticed that according to the HF/6-31+G* calculations in the neutral states of the present molecules the $\pi^*_{N=N}$ MO is not the LUMO, but the fourth or fifth unoccupied MO, in disagreement with the 6-31G** and with (not reported) 3-21G* and semiempirical MNDO results. However, even the 6-31+G* calculations predict that in the most stable anion state the extra electron is accommodated into the $\pi^*_{N=N}$ antibonding MO. Moreover, for the present molecular systems, the results of the 6-31+G* and 6-31G** calculations are quite similar with respect to both the geometry (as mentioned above) and the energy (see Table 3) variations on going from the neutral to the first anion state.

The calculated M−N=N angle is significantly smaller than 120° in all the neutral compounds and is further reduced in the anions, where its value (in the 107°−111° range) approaches the tetrahedral value. As a consequence, the bulky $C(CH_3)_3$ and $Si(CH_3)_3$ groups rotate around the M−N bond (Φ = 60°) to relieve the steric hindrance between their hydrogen atoms and the nitrogen atom bound to the other substituent. Thus, in the anion of **2** and **4** one of the carbon atoms of the methyl groups lies in the main molecular plane anti to the double bond.

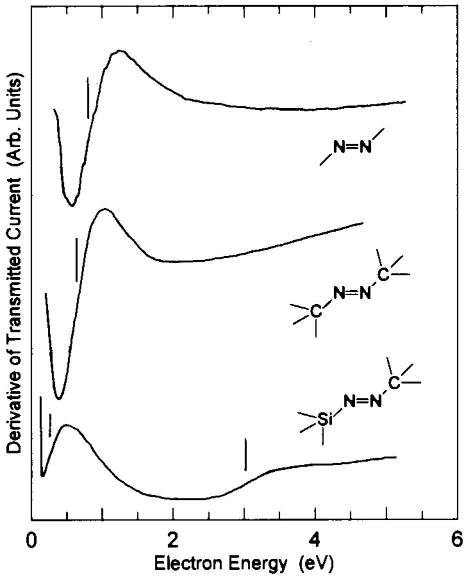

Figure 1. Derivative of the electron current transmitted through gas-phase bis(methyl)diimine (**1**), bis(*tert*-butyl)diimine (**2**), and 1-trimethylsilyl-2-*tert*-butyldiimine (**3**) as a function of the incident electron energy. Vertical lines locate the most probable AE values.

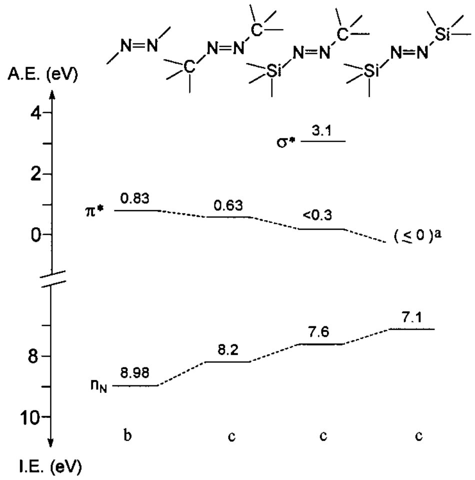

Figure 2. Correlation diagram of the AE and ionization energy values in bis(methyl)diimine (**1**), bis(*tert*-butyl)diimine (**2**), 1-trimethylsilyl-2-*tert*-butyldiimine (**3**), and bis(trimethysilyl)diimine (**4**). (a) Evaluated, see text. Ionization energy values taken from (b) ref 22, (c) ref 1.

The charge distributions calculated in the neutral molecules at the HF/6-31G** level indicate that the negative charge at the nitrogen atoms increases on going from the carbon derivatives **1** and **2** ($q = -0.234e$) to the silicon derivative **4** ($q = -0.404e$), in line with the larger electron-releasing effect of the silyl substituent and with the results of CNDO calculations.[1] In the anions the negative charge at the nitrogen atoms becomes about −0.50 e in **1** and **2** and −0.59e in **4**. The smaller increase of negative charge at the double bond upon anion formation when M = Si confirms the significant localization of the π^* LUMO at the substituents in the silyl derivative (due to σ^*_{Si-C}/π^* mixing), in line with the calculated AE trend and localization properties.

Figure 1 reports the ET spectra of the diimines **1**−**3** in the 0−5 eV energy range. The measured vertical AE values are given in Table 3 and in the correlation diagram of Figure 2, together with the first ionization energy (IE) values. The ET spectrum of bis(methyl)diimine displays a single distinct resonance, centered at 0.83 eV, associated with the $\pi^*_{N=N}$ LUMO. This resonance presents a progression of vibrational structures spaced by about 125 meV (ca. 1000 cm^{-1}), probably due to NN stretching. Owing to the antibonding character of the LUMO, the frequency of this vibrational mode in the first anion state is expected to be sizeably lower than in the neutral state (1580 cm^{-1}).[20] Comparison with the ET spectrum of *trans*-2-butene,[21] where the $\pi^*_{C=C}$ resonance is located at 2.10 eV, reveals that the electron affinity of the N=N double bond is about 1.3 eV higher than that of the ethene C=C double bond.

Electron capture in the LUMO of bis(*tert*-butyl)diimine (**2**) occurs at 0.63 eV; that is, replacement of the methyl groups with *tert*-butyl groups causes an electron affinity increase of about 0.2 eV. The calculations closely reproduce this effect (see Table 3 and Figure 2). A similar stabilization of the π^* resonance was observed on going from the methyl to the *tert*-butyl derivative of ethene.[5] This effect was interpreted in terms of lower energy (and consequently larger σ^*/π^* mixing) of the empty σ^* orbitals of the *tert*-butyl group with respect to the methyl group. A sizably larger stabilization (0.6 eV) of the ethene $\pi^*_{C=C}$ orbital is caused by the trimethylsilyl substituent.[5] In addition, the ET spectrum of trimethylsilylethene displays a second resonance (3.7 eV), ascribed to σ^* orbitals with mainly Si−C character. In agreement, in 1-trimethylsilyl-2-*tert*-butyldiimine (**3**) the $\pi^*_{N=N}$ resonance partially overlaps with the high-energy wing of the intense electron beam signal (see Figure 1). The resulting feature is located at 0.3 eV, which is to be considered as a higher limit for the first AE value. The ET spectrum of **3** also displays a second rather broad resonance, centered at 3.1 eV, associated with electron attachment to σ^*_{Si-C} orbitals. The experimentally observed stabilization ($\geq$0.3 eV) of the $\pi^*_{N=N}$ LUMO upon replacement of a *tert*-butyl substituent with a trimethylsilyl substituent is closely reproduced by the calculations (see Table 3), which predict this effect to be about 0.8 eV upon replacement of both the *tert*-butyl groups. These data thus indicate that bis(trimethylsilyl)diimine **4** must possess a slightly positive electron affinity. For this reason we did not attempt to synthesize sample **4**, given that stable anion states are not accessible in ETS.

Table 3 also lists the adiabatic AE (AE_a) values computed at the ΔSCF (HF/6-31G** and 6-31+G*) levels. The AE_a values are lower than the corresponding vertical values (AE_v) by 0.7, 0.9, and 1.1 eV for the methyl, *tert*-butyl, and trimethylsilyl diimines, respectively. That is, the energy difference between the vibrationally excited and the ground anion states increases in the same direction in which the anion geometry changes with respect to the neutral state as indicated by the Δd_{M-N} and Δ_{M-N-N} values (see Table 3): namely, **1** < **2** < **4**.

Comparison of the present results with those obtained by means of photoelectron spectroscopy (see Figure 2) demonstrates that the EA increase ($\approx$0.4 eV) caused by each silyl substitution is not much smaller than the IE decrease ($\approx$0.5 eV). In particular, the hardness (η), which reflects the HOMO−LUMO energy gap, as evaluated[23] from $\eta = (\mathrm{IE} - \mathrm{EA})/2$, gradually decreases along the series: 4.9 (**1**), 4.4 (**2**), 3.9 (**3**), and $\approx$3.5 (**4**) eV. The above-mentioned large reduction (1.8 eV) of the HOMO−LUMO transition energy on going from bis(*tert*-butyl)diimine to bis(trimethylsilyl)diimine is therefore to be ascribed to the concomitant energy perturbations produced on both the filled and empty orbitals involved.

Acknowledgment. The authors thank the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica for financial support.

References and Notes

(1) Bock, H.; Wittel, K.; Veith, M.; Wiberg, N. *J. Am. Chem. Soc.* **1976**, *98*, 109.

(2) Modelli, A. *Trends Chem. Phys.* **1997**, 6, 57.

(3) Modelli, A.; Jones, D.; Favaretto, L.; Distefano, G. *Organometallics* **1996**, *15*, 380.

(4) Modelli, A.; Scagnolari, F.; Distefano, G.; Dal Colle, M. *J. Organomet. Chem.* **1997**, 549, 149.

(5) Modelli, A.; Jones, D.; Distefano, G. *Chem. Phys. Lett.* **1982**, 86, 434.

(6) Modelli, A.; Distefano, G.; Jones, D.; Seconi, G. *J. Electron Spectrosc. Relat. Phenom.* **1983**, 31, 63.

(7) Sanche, L.; Schulz, G. J. *J. Phys. Rev.* A **1972**, 5, 1672.

(8) Johnston, A. R.; Burrow, P. D. *J. Electron Spectrosc. Relat. Phenom.* **1982**, 25, 119.

(9) Wiberg, N.; Veith, M. *Chem. Ber.* **1971**, *104*, 3176.

(10) Wiberg, N.; Veith, M. *Chem. Ber.* **1971**, *104*, 3191.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*, Revision D4; Gaussian, Inc. Pittsburgh PA, 1995.

(12) Almenningen, A.; Anfinsen, I. M.; Haaland, A. *Acta Chem. Scand.* **1970**, *24*, 1230.

(13) Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 5313.

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Braammer, L.; Guy Orpen, A.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(15) *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993.

(16) Veith, V. M.; Barnighousen, H. *Acta Crystallogr.* B **1974**, 30, 1806.

(17) Almenningen, A.; Tjeldberg, T.; Henge, E. *J. Mol. Struct.* **1984**, 112, 239.

(18) Guerra, M. *Chem. Phys. Lett.* **1990**, 167, 315.

(19) Heinrich, N.; Koch, W.; Frenking, G. *Chem. Phys. Lett.* **1986**, 124, 20.

(20) Durig, J. R.; Pate, C. B.; Harris, W. C. *J. Chem. Phys.* **1972**, 56, 5652.

(21) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *Chem. Phys. Lett.* **1976**, 42, 227.

(22) Houk, K. N.; Chang, Y.-M.; Engel, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 1824.

(23) Pearson, R. G. *Acc. Chem. Res.* **1993**, *26*, 250.