Reinvestigation of the Formaldehyde–Aniline Condensation. Part 4.[1] Ultraviolet Photoelectron and Electron Transmission Spectra of *N*-Methyleneaniline and its Symmetric Dimethyl Ring-substituted Homologues and Semiempirical Theoretical Evaluations

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A study of the vapours over heated 1,3,5-triphenylhexahydrotriazine (III) has been made by u.v. photoelectron and electron transmission spectral techniques. Complementary data are also reported for the homologous derivatives 2,2′,2″,6,6′,6″- and 3,3′,3″,5,5′,5″-hexamethyl-1,3,5-triphenylhexahydrotriazines. The vapours over these compounds are found to be made up mostly of monomeric *N*-methyleneaniline (I) and of its dimethyl derivatives, respectively. The ionization and electron affinity data are compared with those of reference molecules. Theoretical MO energies obtained by means of an MNDO program for optimized geometries of (I), its dimer 1,3-diphenyldiazetidine (II), and of the references molecules are compared with the experimental data. It appears that, in the gas phase (*ca.* 100 °C and 0.0001 Torr) (I) and its dimethyl derivatives adopt a conformation characterized by a strong π(ring)–π(NC) mixing, that is, a nearly coplanar conformation.

N-Methyleneaniline (I) is an elusive compound. Although a recent patent claimed its preparation in the pure crystalline state,[2] the misidentification is all too obvious: the substance otained was the now[3] well established cyclic trimer (III), which can be obtained under a variety of experimental conditions from aqueous formaldehyde or a solid derivative of formaldehyde, *i.e.* paraformaldehyde, and aniline. This reaction may produce significant amounts of a cyclic tetramer, a higher melting compound, whose structure has been recently established.[1] There have been claims[4] for a cyclic dimeric product (II), but they were dismissed.[3] On the other hand, there is some indication that both (I) and (II) might exist in equilibrium with (III). In addition to molecular weight determinations in solution which misled some authors,[4,5] yielding too low values for (III), many chemical reactions seem to involve free (I) and (II) (not necessarily in the cyclic form shown here). The trimer (III) surprisingly boils at 185 °C at 760 Torr, and gas chromatography and mass spectrometry[3] indicate the presence of a large concentration of (I) [and a smaller one of (II)] in the gas phase over (III).

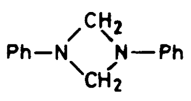
Compounds (I) and (II) are of great interest. The former offers a simple instance of competitive conjugation of the aromatic π-system with the nitrogen lone pair or with the exocyclic double bond, with obvious structural consequences. The latter is a case of a strained ring system for which there are no similar compounds reported authoritatively and conclusively.

N-Methyleneaniline (I) is expected to be a reactive compound, which could well be used as a synthon in many important synthetic processes. However, experimental data on its geometry and electronic structure have not been reported.

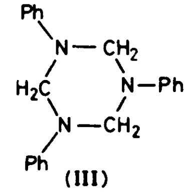
The aim of the present investigation is to characterize spectroscopically, and in terms of a simplified MO description, a series of three closely related *N*-methyleneanilines. For this purpose, u.v. photoelectron spectroscopy (UPS)[6] and electron transmission spectroscopy (ETS)[7] were chosen as experimental tools, since they measure ionization energies (IEs) and electron affinities (EAs), respectively. These data provide a very sensitive description of the occupied and empty energy level patterns and reflect conformational properties.[8,9]

$Ph—N=CH_2$

(I)



(II)



(III)

The corresponding compounds derived from 2,6- and 3,5-dimethylaniline were also investigated. In fact, the electronic effects exerted by the methyl groups in these two compounds are very similar, while in the *o,o′*-derivative steric hindrance could cause the rotation of the $-N=CH_2$ group out of the ring plane, reducing the π(ring)–π(NC) electronic interaction.

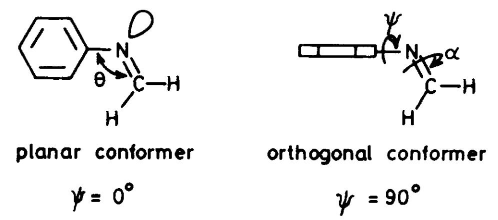
As a theoretical counterpart a program based on the MNDO Hamiltonian of Dewar and Thiel[10,11] was adopted, since it is known to provide reliable estimates of ionization energy values.

Experimental and Computations

Trimer (III) was prepared as described.[3] The synthesis of its 2,6- and 3,5-dimethyl derivatives will be described elsewhere.[12]

Our ETS apparatus is in the format devised by Sanche and Schulz[7] and has been described previously.[13] Briefly, an electron beam, selected in energy by a trochoidal monochromator and aligned by a magnetic field, is directed through a gas-filled collision chamber. A retarding voltage is responsible for the rejection of those scattered electrons which have lost a given amount of axial velocity. By setting this voltage close to that of the filament, a nearly total scattering cross section is observed.[14]

In order to enhance sharp variations in the cross-section associated with resonance, the first derivative of the electron current transmitted to the collector is recorded as a function of the electron-impact energy. This is achieved by modulating the



electron energy with a small alternating current voltage in the collision region and employing a synchronous lock-in amplifier.

The main limitation of ETS is that stable anion states (that is, in a Koopmans' theorem sense, those anion states which are associated with empty orbitals lying below zero energy) escape detection.

The quoted attachment energies (AEs) are taken as the vertical midpoints between the minima and the maxima of the derived signal and closely approximate the negative of the vertical EAs. The ($1s\ 2s^2$) ^2S anion state of He was used for the calibration of the energy scales.

The photoelectron spectra were recorded on a Perkin-Elmer PS18 spectrometer and calibrated against the Xe and Ar lines.

The estimated accuracy of the AE and IE values is ±0.05 or ±0.1 eV, depending on the number of significant figures reported.

For MO calculations, two programs were utilized. The first, based on the INDO/2 Hamiltonian of Pople and Beveridge,[15] was applied to the preliminary investigation of the conceivable limiting structures of (I), characterized by the following three variables: θ, the C–$\hat{N}$–C angle; ψ, the dihedral angle between the plane of the ring and the plane containing the ring *ipso*-position, the N atom, and the methylene C atom; α, the angle of rotation of the CH_2 plane around the *N*-methylene carbon bond. INDO screening, carried out with a limited optimization of the crucial bond lengths and angles, showed that out of the possible combinations (θ 120, 180°; ψ 0, 90°; α 0, 90°) those having θ 120°; ψ 0, 90°; α 0° were greatly preferred over the others, *i.e.* those characterized by essentially sp^2 nitrogen atom hybridization and having the CH_2 group either coplanar with the ring or perpendicular to it.

The MNDO investigation was carried out with the central section of the QCPE Program Package No. 428, *i.e.* the part concerned with the localization of minima on energy hypersurfaces. Optimization of the two preferred limiting structures predicted by INDO/2, and of the intermediate structures having ψ 10, 20, ... 80°, followed. The phenyl ring was constrained to planarity, while the other internal co-ordinates were allowed to relax.

Various conformations were examined for molecule (II). The variables considered were the CH_2–$\hat{N}$–CH_2 angle, the angle between the two planes each containing one nitrogen atom and the two methylene carbon atoms, and the angle of rotation of the phenyl ring around the C(ring)–N direction. The preferred conformation appears to be the all-planar one and its energy lies below that of a pair of molecules (I) both in their planar or in their perpendicular conformation, with an energy gain of 10 kcal mol^{-1} with respect to (I) in the planar form.

Calculations were performed on a VAX 11/780 Digital Equipment Corporation computer of the Theoretical Chemistry Group, Bologna.

Results and Discussion

The He^I UP and ET spectra of the vapour of (III) [mainly in its monomeric form (I), see below] and of its 2,6- and 3,5-dimethyl analogues are reported in Figures 1 and 2, respectively. The first two samples were heated to *ca.* 100 °C, the third to *ca.* 60 °C.

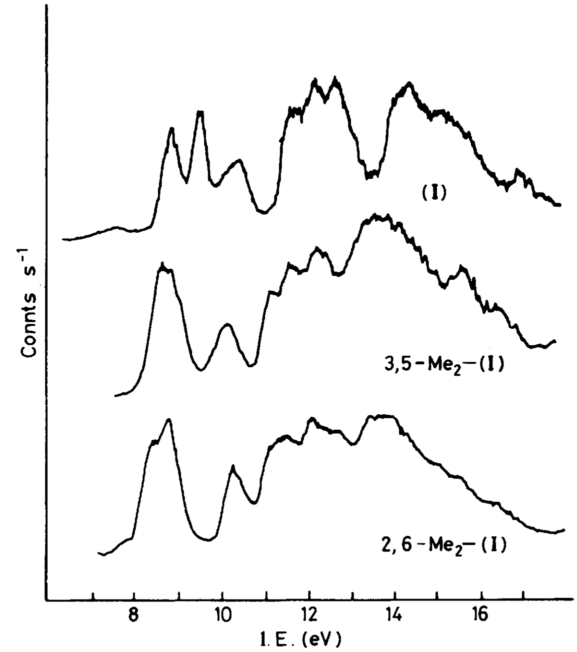


Figure 1. He^I photoelectron spectra of the vapour of (III) [mainly in its monomeric form (I)] and of its 3,5- and 2,6-dimethyl analogues

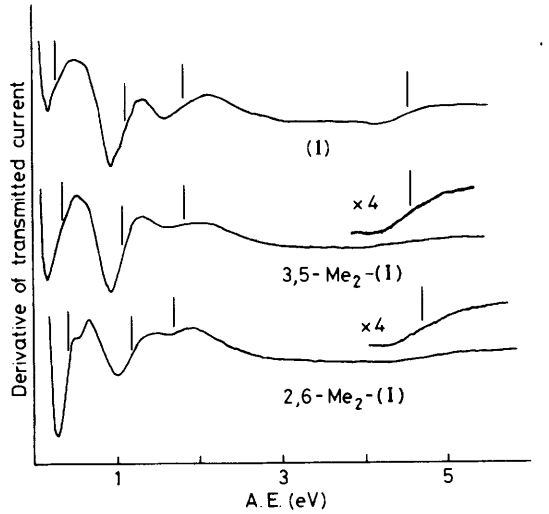


Figure 2. Electron transmission spectra of the vapour of (III) [mainly in its monomeric form (I)] and of its 3,5- and 2,6-dimethyl analogues

The UP spectra of these compounds show three intense peaks in the low IE range (< 10.5 eV), flanked by a broader envelope of bands at higher IE.

The ET spectra are very similar to each other and display four* resonances in the 0—5 eV energy range. The first resonance of the vapour of (III), and to a lesser extent the corresponding resonance of its 3,5-dimethyl derivative, is partially superimposed on the wings of the signal from the electron beam. The measured values of 0.25 and 0.32 eV,

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* The weak feature partially overlapped with the first resonance in the spectrum of 2,6-dimethylmethyleneaniline is most likely due to vibrational fine structure.

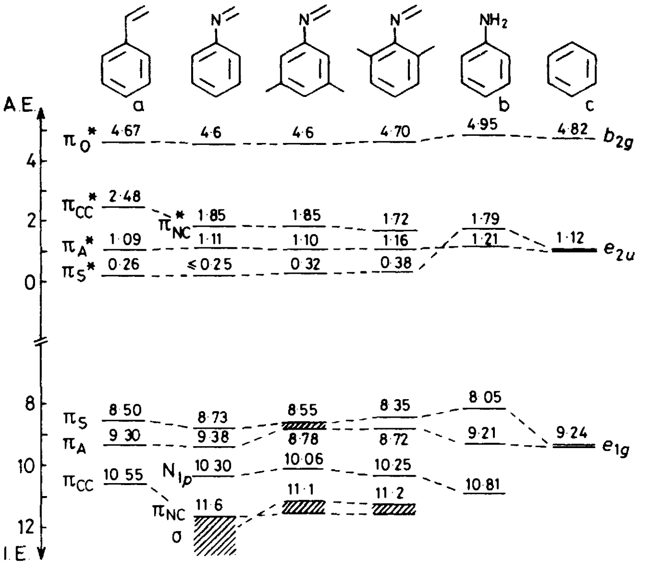

Figure 3. IEs and AEs of styrene, *N*-methyleneaniline (I), 3,5- and 2,6-dimethyl-*N*-methyleneaniline, aniline, and benzene, as determined by means of UPS and ETS: a, AEs from ref. 19; IEs from ref. 17; b, AEs from ref. 19; IEs from ref. 18; c, AEs from ref. 13; IEs from ref. 6

respectively, can thus be considered upper bounds to the first AE of the two compounds.

The planar (ψ 0°) conformer of (I) characterized by π(ring)—π(NC) conjugation, can be thought of as a styrene molecule † in which an ethylene CH group has been replaced by a nitrogen atom. The orthogonal (ψ 90°) conformer, in contrast, is characterized by mixing between the ring π-system and the nitrogen lone pair orbital (N_{1p}). Its π-electron structure is thus expected to be similar to that of aniline.

In Figure 3 the IE and AE data for the compounds under examination are reported and compared with those of benzene, styrene, and aniline.

We briefly recall that in styrene[17] and aniline[18] the highest occupied MO (HOMO, π_S) has a large contribution from the benzene e_{1g} component with a maximum of charge density at the substituted carbon atom, the second occupied MO (π_A) is essentially the benzene e_{1g} component with a node at the *ipso*-position (IE 9.24 eV in benzene[6]), and the third occupied MO [π(C=C) in styrene and N_{1p} in aniline] are mainly ethylene and N_{1p} in character, respectively.

A larger differentiation is found when the empty levels of the two molecules[19] are compared, the unoccupied π*(C=C) MO (AE 1.73 eV in ethylene[20]) having no counterpart in the NH_2 group.

In styrene the degeneracy of the empty benzene e_{2u} (π*) MO (AE 1.12 eV in benzene[13]) is removed by admixture of the component of proper symmetry with the π*(C=C) orbital. The AE (0.26 eV) of the resulting lowest unoccupied MO (LUMO, π_S^*) is much lower than that (1.09 eV) of the nearly unperturbed e_{2u} component (π_A^*). The third and fourth MOs [π*(C=C) and π_0^*, AEs 2.48 and 4.67 eV] have predominant ethylene and benzene b_{2g} (π*) character, respectively.

In aniline only three empty π* MOs are present The benzene e_{2u} component of appropriate symmetry is sizeably destabilized by charge-transfer interaction with the filled N_{1p} orbital, the b_{2g} MO (4.82 eV in benzene[13]) being destabilized to a lesser extent.

On going from styrene to the planar form of (I), the replacement of a CH group with a more electronegative nitrogen atom is expected to cause stabilization of the filled and empty MOs, which must increase with their wave function coefficients at the site of substitution. Besides, one more filled MO, the N_{1p} (σ) MO (9.6 eV in pyridine[21]), is expected in the low IE region.

The perpendicular conformer of (I) has two MOs not present in aniline, namely the filled π(NC) and the empty π*(NC) orbitals, which do not mix with the ring π-system. In the UP spectrum, the signal from the former could not be resolved from the broad bands arising from the σ-framework. In contrast, the resonance associated with the π*(NC) MO, expected at *ca.* 1.29 eV as in 1,1-di-t-butylimine,[22,‡] should characterize the ET spectrum.

Examining now the IEs and AEs of the vapour of (III) and correlating them with those of styrene, we are led to attribute both the UP and ET spectra of this compound to monomer (I), in a conformation which allows strong conjugation between the imine and benzene fragments.

In fact, the replacement of the ethylene CH group with a nitrogen atom (see Figure 3) does not affect the energies of the π_A and π_A^* MOs, which are essentially localized on the benzene ring; the HOMO, the LUMO, and the π_0^* MO, with prevailing ring character, are slightly stabilized; the π(C=C) and π*(C=C) MOs, with large wavefunction coefficients at the sites of substitution, are much stabilized, in agreement with the predictions for the planar conformation.

In particular, the low-energy (0.25 eV) resonance, associated with the LUMO (π_S^*), supplies clear evidence for strong π*(NC)–π*(ring) conjugation. In the perpendicular form, the LUMO would be π_A^*, at *ca.* 1 eV higher energy.

The peak at 10.3 eV in the UP spectrum is correlated with the N_{1p} (σ) MO. In the perpendicular form of (I) the IE of this MO should be close to that of the corresponding MO of aniline (10.81 eV).

The weak band centred at 7.45 eV (see Figure 1) is somewhat temperature dependent and will be discussed below.

We note that the stabilization of the filled π(C=C) MO is about twice as large as that of the empty π*(C=C) MO, in spite of the similar double-bond character of the two MOs. This is consistent with a previous ET study of pyridine derivatives,[19] where the smaller effect experienced by the empty MOs upon N for CH substitution has been explained in terms of the C–N bond length being shorter than the C–C bond length. This geometrical variation is destabilizing for the antibonding orbitals and partially compensates for the stabilizing effect of the nitrogen atom.

The IE and AE data for the products of the reactions of 3,5- and 2,6-dimethyl-*N*-methyleneaniline with paraformaldehyde are given in Figure 3 and can be easily correlated with those of monomer (I). Mixing with the σ_{CH_3} orbitals destabilizes the σ(ring) MOs and the N_{1p} (σ) MO. Hyperconjugation with the σ_π orbitals of the CH_3 groups destabilizes the HOMO (π_S) and, to a larger extent due to its larger wavefunction coefficients at the sites of substitution, the second occupied MO (π_A), so that the UPS signals associated with the two MOs are barely resolved.

In agreement with previous ETS studies,[19,23] the net electronic effect of the methyl groups on the empty ring π* MOs is very small (this is confirmed by the MO calculations).

When the IEs and the AEs of the 3,5- and 2,6-dimethyl derivatives are compared, in the latter an increase of the energy

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† According to Raman studies,[16] in styrene the ring and ethylene fragments are coplanar.

‡ The t-butyl group causes a small energy perturbation on adjacent empty π* MOs, due to the opposite hyperconjugative effects of its filled σ_π and empty σ_π^* orbitals.[13,23]

Table. Comparison between experimental AEs and IEs and theoretical orbital energies calculated by MNDO

Benzene		Experiment	Theory
	b_{2g}	4.82	2.68
	e_{2u}	1.12	0.37
	e_{1g}	9.24	−9.39
Styrene			
	π_O^*	4.67	2.75
	π_{CC}^*	2.48	1.50
	π_A^*	1.09	0.37
	π_S^*	0.26	−0.12
	π_S	8.50	−8.82
	π_A	9.30	−9.41
	π_{CC}	10.55	−10.71
Aniline			
	π_O^*	4.95	2.58
	π_S^*	1.79	0.31
	π_A^*	1.21	0.34
	π_S	8.05	−8.75
	π_A	9.21	−9.46
	N_{1p}	10.81	−11.47

N-Methyl-eneaniline (I)		Experimental	Theory	
			ψ 0°	ψ 90°
	π_O^*	4.6	2.77	2.56
	π^*_{NC}	1.85	1.54	0.93
	π_A^*	1.11	0.30	0.31
	π_S^*	0.25	−0.27	0.25
	π_S	8.73	−9.06	−9.00
	π_A	9.38	−9.50	−9.47
	N_{1p}	10.30	−10.66	−11.23
	π_{NC}	11.60	−11.91	−11.64
1,3-Diphenyl-diazetidine (II)				
			2.04	σ^*
			1.74	σ^*
			0.54	π_S^{*-}
			0.46	π_S^{*+}
			0.39	π_A^{*-}
			0.34	π_A^{*+}
		7.45(?)	−8.36	π_S^+
			−8.41	π_S^-
			−9.38	π_A^+
			−9.43	π_A^-
			−10.73	N_{1p}^-
			−11.32	N_{1p}^+

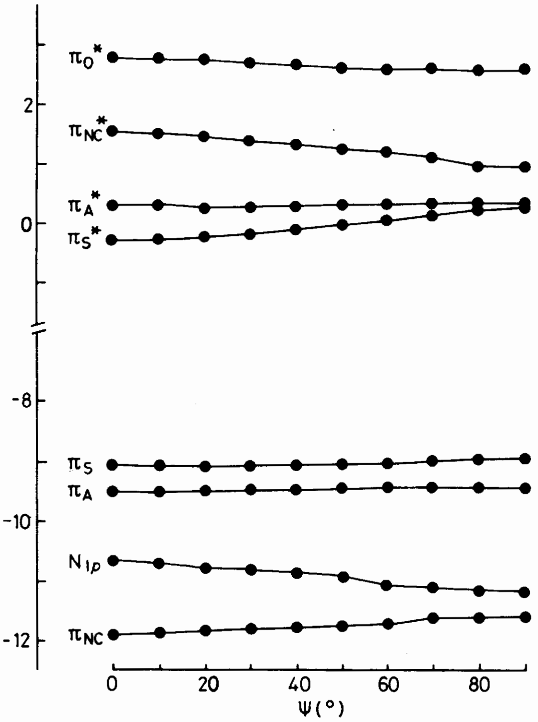

Figure 4. MNDO orbital energies for *N*-methyleneaniline (I) as a function of the dihedral angle ψ

separation between the filled π_s and N_{1p} MOs and a decrease of the energy separation between the empty π_S^* and π*(NC) MOs are observed. This is consistent with an increase of the N_{1p}–π (ring) interaction and a concomitant reduction of π (NC)–π(ring) conjugation, that is, with deviation from coplanarity between the two π systems, due to steric hindrance, in 2,6-dimethyl-*N*-methyleneaniline. However, this effect is small, and, in particular, by far smaller than that observed in 2,6-dimethylstyrene.[17] A larger C$\hat{N}$C angle in (I), with respect to the corresponding CCC angle in styrene (according to the present calculations 128 and 122°, respectively), is a possible explanation for the reduced steric hindrance caused by *o,o'*-dimethyl substitution in the former molecule.

The weak shoulder in the low IE range (7.8 eV) of the spectrum of 2,6-dimethyl-*N*-methyleneaniline (see Fig reu1) could indicate the presence of a small amount of the rotated conformer, whose IE is predicted to be close to that (7.85 eV[18]) of 2,6-dimethylaniline. However, the presence of 2,6-dimethylaniline itself (which is one of the reagents) as an impurity cannot be ruled out.

As far as dimer (II) is concerned, its HOMO can be considered to be derived from in-phase combination between the HOMOs of the two aniline moieties. This orbital is destabilized by hyperconjugation with the in-phase combination of the σ_π MOs of the CH_2 groups. Its energy, therefore, should not differ very much from that of the HOMO of *NN*-dimethylaniline (IE 7.45 eV[18]).

The weak signal observed at 7.45 eV in the spectrum of (I) could thus arise from (II) [and/or (III)]. This is consistent with the mass spectrum of (III),[3] which shows weak peaks at *m/e* 210 and 315 [the *m/e* values of the molecular ions of (II) and (III)].

ETS has shown that the energies of the corresponding empty π* MOs of aniline,[19] *N*-methylaniline,[24] and *NN*-dimethylaniline[25] are very similar. The empty π* orbitals of (II) and (III) should therefore be close in energy to those of aniline and the detection of traces of these compounds in the ET spectrum would be prevented by the last three resonances of (I).

Comparison with Theoretical Results.—The Table reports the energies calculated for the frontier MOs of (I) in both the planar and perpendicular forms, of dimer (II), and of benzene, styrene, and aniline. The values for the dimethyl-substituted compounds are not included since they do not provide much additional information. As far as the filled MOs of the three reference molecules are concerned, the calculated energies are close to the negative of the experimental IEs. On the other hand, the computed energies of the empty MOs are significantly lower than the measured AEs, the discrepancy increasing with the energy of the MO considered. In addition, the present calculations undervalue the N_{1p}–π^* change-transfer interaction (which causes a sizeable destabilization of the π_S^* MO) observed in the ET spectrum of aniline.

Figure 4 shows the calculated MO energy levels of (I) as a function of the dihedral angle ψ. The energy of the first two occupied MOs decreases only slightly from ψ 0 to 90°, their values being close to the negative of the corresponding IEs (see Table).

In contrast, the third MO, mainly N_{1p} in character, is much stabilized on going from the planar to the perpendicular form, while the energy of the fourth occupied MO [π(NC)] changes in the opposite direction. Both the energy of the N_{1p} MO (−10.66 eV) and the N_{1p}–π(NC) energy separation (1.3 eV) calculated for the planar form match well the experimental values (10.3 eV and 1.3 eV, respectively). In contrast, according to the calculations, in the perpendicular form the N_{1p}–π(NC) energy separation is only 0.4 eV and the N_{1p} MO (*ca.* 1 eV more stable than in the planar form) is close in energy to that of the corresponding MO in aniline, as predicted in the above discussion on qualitative grounds.

As far as the empty levels are concerned, the energy trend calculated for the planar conformer reproduces the experimental one. The computations on the perpendicular conformer suffer from the same limitations noticed for aniline, showing an inadequate destabilization of the π_S^* ring orbital by interaction with the N_{1p} orbital (see Figure 4 and Table). They, however, support the expectation that the ET spectrum of the perpendicular form of (I) should be similar to that of aniline, with an additional resonance, associated with the π*(NC) MO, at slightly higher energy than that of the π* MO.

The comparison between the experimental and computational energy levels confirms, therefore, that monomer (I), in a conformation allowing strong π (NC)–π(ring) mixing, is the most abundant species in the vapour of (III).

The MNDO analysis of (I) showed also that the total energy and the negative charge on nitrogen slightly depend on the dihedral angle ψ and decrease monotonically with increasing ψ value. In addition, the rotational barrier around the C(ring)–N bond (1.5 kcal mol^{-1}) is rather smaller than that (*ca.* 3 kcal mol^{-1}) obtained by *ab initio* calculations.[26] These data suggest a nearly free rotation about the C(ring)–N bond with a preference for the orthogonal conformation, in contrast with the prediction of the orbital energy pattern and experimental evidences.

Turning now to dimer (II), the calculations confirm (see Table) that its HOMO is much destabilized with respect to the HOMO of both monomer (I) and aniline, supporting the above assignment to (II) and /or (III) of the weak peak at 7.45 eV in the UP spectrum of the vapour of (III).

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