Nonempirical Investigations on the Azomethine Group. 1. The Effect of the Conjugation with a Phenyl Ring. A Comparison of the Electronic Structure of the Ground and Lowest Excited States in Benzaldimine and *N*-Phenylformaldimine

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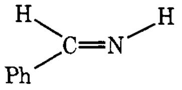
Abstract: The possibility of differential effects due to conjugation with a phenyl ring when linked either to the C or N end of the azomethine group is investigated by means of ab initio calculations on the ground and lowest excited states of benzaldimine (**1**), *N*-phenylformaldimine (**2**), and the parent compound methylenimine. For the description of the excited states, the electron-hole potential method by Morokuma and Iwata has been adopted. Population analysis shows that the ability of the azomethine group to accept or to donate electrons in a given state is practically the same in molecules **1** and **2**. A parallel analysis of the electrostatic molecular potential confirms the results of the population analysis and in addition shows differences in reactivity between the two molecules in a given state and among the various states in each molecule.

Introduction

Relatively little nonempirical theoretical work has been done thus far for the study of the spectrum and the structure of excited states of molecules containing the azomethine >C=N– group.[2] This apparent lack of interest is perhaps due to the relative scarcity of experimental data on these compounds, although there are in the literature examples of interesting and peculiar behaviors of azomethines, some of which have not yet received a satisfactory interpretation.

A specific question which, according to our knowledge, has not received much attention is that of the different behavior of related molecules having the C or the N atom linked to a π system. As a conclusion of an experimental work on the absorption spectra of *N*-benzylimines, El-Aasser et al.[3] state that "the azomethine group acts as an electron acceptor when linked to a phenyl group at its carbon end and as an electron donor when linked to a phenyl group at its nitrogen end".

In the present paper we will try to see whether ab initio calculations on the simpler compounds of these two sets, benzaldimine (**1**) and *N*-phenylformaldimine (**2**), confirm this interpretation.



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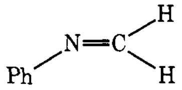

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These compounds can be considered as representative examples of a larger class characterized by the occurrence of a chromophore (>C=N– in the present case) which interacts with a second one (the phenyl ring). As will be shown later, the combination of the method employed to get the wave function of the excited state and the basis set adopted for the calculations permits discrimination between the transitions belonging to the first chromophore and those having a composite character. In the analysis performed in the present paper we have made use of the examination of the electrostatic molecular potential. We feel confident that such an approach will result in also being helpful for the interpretation of the excited electronic states in other molecules.

Method

For the determination of the lowest excited electronic states we have employed the electron-hole potential (EHP) method proposed by Morokuma and Iwata.[4] The starting point of this method is given by the SCF-MO set of the ground state. By means of a variational procedure, the method determines the best definition of a hole ϕ_α (expanded within the occupied MO's subspace) and of a particle ϕ_μ (expanded within the virtual MO's subspace) which minimizes the energy for the state corresponding to the single substitution electronic excitation ($\alpha \rightarrow \mu$). The excited states are orthogonal to the ground one, with wave functions satisfying some extensions of the Brillouin theorem. According to a recently proposed classification scheme of the ab initio methods to compute excited state wave functions,[5] the EHP method is considered as an "improved" ground-state molecular orbital (IGSMO) method because occupied and virtual canonical orbitals are allowed to adjust themselves, within their subspaces, to take account of the electron excitation.

We shall consider only vertical transitions: the geometrical parameters we have adopted correspond to an idealized geometry for the two molecules.[6] The calculations have been performed with the STO-3G minimal basis set supplemented with a set of s and p diffuse Gaussians on the C and N atoms of the azomethine group (basis set STO-3G + sp) with orbital exponents 0.06 and 0.1, respectively. As a check, the calculations have been repeated using the STO-3G set alone.

Results

The ordering of the orbital levels in the ground state is reported in Table I for the two molecules and the two basis sets. The orbital description of the ground state is quite similar for the two molecules. The two highest occupied orbitals (4b and 3b) are π orbitals on the ring, with some admixture from the π orbital of the azomethine group. The next one, going to more negative energies, is a nearly pure N lone pair (24a), and it is followed in both molecules by a π orbital (2b) where the components from the C=N group represent a little more than half of its total charge distribution. The ring contributions are slightly larger in molecule **2** than in **1**. The lowest π orbital (1b) is decidedly more stabilized and can be described as a combination of the C=N π orbital with the lowest lying π orbital of the ring. There are no great differences in the description offered by the two basis sets.

Appreciable differences do on the contrary appear in the virtual manifold. In the STO-3G basis, the three lowest un-

Table I. Energies[a] of the Highest Occupied and Lowest Virtual Orbitals of Benzaldimine (**1**), *N*-Phenylformaldimine (**2**), and Methylenimine (**3**)

1				**2**				**3**			
STO-3G		STO-3G + sp		STO-3G		STO-3G + sp		STO-3G		STO-3G + sp	
1b	−12.96	1b	−13.72	1b	−13.19	1b	−13.90				
22a	−12.03	22a	−12.64	22a	−12.50	22a	−12.91				
23a	−11.79	23a	−12.35	23a	−12.15	23a	−12.58				
2b	−10.93	2b	−11.82	2b	−11.02	2b	−11.80				
24a	−9.11	24a	−10.25	24a	−8.90	24a	−10.13				
3b	−7.61	3b	−8.10	3b	−7.82	3b	−8.15	1b	−10.21	1b	−12.00
4b	−7.17	4b	−7.87	4b	−7.34	4b	−7.75	7a	−9.37	7a	−11.09
5b	6.01	5b	3.93	5b	6.02	5b	3.01	2b	7.80	2b	2.83
6b	7.26	25a	4.06	6b	7.04	25a	4.53	8a	17.00	8a	3.61
7b	9.90	26a	5.45	7b	9.54	26a	4.82			9a	4.30
8b	14.11	6b	6.27	8b	13.76	27a	6.04			10a	4.86
25a	15.88	7b	6.80	25a	14.96	6b	6.42			3b	7.33
		27a	7.21			7b	6.86			11a	9.73
		8b	8.67			8b	9.16			4b	11.87
		28a	10.68			28a	12.44				
		29a	12.53			9b	13.18				
		9b	13.17			29a	13.57				

[a] eV.

Table II. Vertical Excitation Energies,[a] Oscillator Strenghs, and Total Ground State Energies[b]

	Molecule **1**				Molecule **2**			
	STO-3G		STO-3G + sp		STO-3G		STO-3G + sp	
	ΔE	f	ΔE	f	ΔE	f	ΔE	f
$^{1}A' \rightarrow {}^{1}A''^{1}$ (n → π*)	5.66	0.008	6.11	0.006	5.80	0.006	5.39	0.003
$^{1}A' \rightarrow {}^{1}A'^{1}$ (π → π*)	8.72	0.958	7.49	0.848	8.82	1.095	6.48	0.490
$^{1}A' \rightarrow {}^{1}A''^{1}$ (π → σ*)	16.61	0.006	7.81	0.003	14.89	0.008	8.45	0.017
$^{1}A' \rightarrow {}^{3}A''^{3}$ (n → π*)	4.28		5.15		4.53		4.41	
$^{1}A' \rightarrow {}^{3}A'^{3}$ (π → π*)	4.89		4.69		4.97		4.11	
$^{1}A' \rightarrow {}^{3}A''^{3}$ (π → σ*)	16.44		7.71		14.20		8.32	
Ground state energy	−319.574 53		−319.697 79		−319.571 48		−319.671 42	

[a] eV. [b] hartrees.

occupied orbitals are of π symmetry and localized on the ring, followed by another π orbital (8b) displaying some C=N character. In the STO-3G + sp manifold, the energy gap is decidedly lower, and the three lowest orbitals (5b, 25a, 26a) are fairly localized on the azomethine. As a comparison we have added in Table I the ordering of the orbital levels in the parent compound methylenimine (**3**, $H_2C{=}NH$) with both basis sets. In this case too, the inclusion of diffuse functions noticeably lowers the energy of the first virtual orbitals, bringing, as a consequence, a difference in their spatial extension with respect to the corresponding ones in the STO-3G basis set.[7] Orbitals 2b, 8a, 9a are fairly similar to the abovementioned orbitals 5b, 25a, 26a of **1** and **2**.

The vertical transition energies to the lowest (n → π*), (π → π*), and (π → σ*) states are reported in Table II. For comparison, the excitation energies of the parent compound, methylenimine (**3**), are reported in Table III. In the following discussion, for brevity, we shall give more emphasis to the singlet states, because there is, to the best of our knowledge, a complete lack of experimental data concerning the forbidden vertical transitions to triplet states. The essential results concerning triplets are, however, reported and more information can be obtained upon request to the authors.

Although the aim of the present work is not addressed to an accurate prediction of the vertical transition energies, it may be of some interest to compare the results of Table II and III with the available experimental data. The discussion is simpler for the methylenimine molecule. The value of 5.20 eV for ^{1}(n → π*) appears to be in good agreement with the experimental values found in unconjugated azomethines (5.25 eV as suggested by Bonnett[8]). The most prominent band in the spectrum of alkylazomethines is usually assigned to the ^{1}(π → π*) transition;[9] the experimental values range in the interval 7.3–6.9 eV decidedly lower than the value of 11.18 eV reported in Table III.

Table III. Vertical Transition Energies,[a] Oscillator Strengths, and Total Ground State Energy[c] for Methylenimine

	STO-3G		STO-3G + sp		4-31G[b]
	ΔE	f	ΔE	f	ΔE
$^{1}A' \rightarrow {}^{1}A''^{1}$ (n → π*)	5.44	0.008	5.20	0.006	5.84
$^{1}A' \rightarrow {}^{1}A'^{1}$ (π → π*)	13.56	1.050	10.18	0.616	10.33
$^{1}A' \rightarrow {}^{1}A''^{1}$ (π → σ*)	16.80	0.000	9.57	0.202	
$^{1}A' \rightarrow {}^{1}A'^{1}$ (n → σ*)			8.57	0.025	
$^{1}A' \rightarrow {}^{3}A''^{3}$ (n → π*)	3.94		4.07		4.68
$^{1}A' \rightarrow {}^{3}A''^{3}$ (π → π*)	3.38		3.93		4.57
$^{1}A' \rightarrow {}^{3}A''^{3}$ (π → σ*)	15.66		9.10		
$^{1}A' \rightarrow {}^{3}A'^{3}$ (n → σ*)			8.17		9.59
Ground state energy	−92.811 86		−92.921 51		−93.8824

[a] eV. [b] From ref 2a. [c] hartrees.

Iwata and Morokuma[10] found it expedient to adopt a refinement of the EHP method to get a better representation of

Table IV. TCEHP Values for the $^1(\pi \rightarrow \pi^*)$ Vertical Transition Energies of Methylenimine in the STO-3G + sp basis

Configuration	ΔE^a	C_1	C_2
$C_1(1b \rightarrow 2b) + C_2(7a \rightarrow 8a)$	8.57	0.0294	0.9996
$C_1(1b \rightarrow 2b) + C_2(7a \rightarrow 10a)$	9.43	0.9595	0.2818
$C_1(1b \rightarrow 2b) + C_2(6a \rightarrow 8a)$	9.45	0.9735	−0.2285

^{a} eV.

Table V. CSECI Values for the Vertical Transition Energies for Methylenimine in the STO-3G + sp Basis

State	ΔE^a	State	ΔE^a
$^1(n \rightarrow \pi^*)$	5.16	$^3(n \rightarrow \pi^*)$	4.03
$^1(\pi \rightarrow \pi^*)$	8.91	$^3(\pi \rightarrow \pi^*)$	3.82
$^1(\pi \rightarrow \sigma^*)$	9.55	$^3(\pi \rightarrow \sigma^*)$	9.05
$^1(n \rightarrow \sigma^*)$	8.51	$^3(n \rightarrow \sigma^*)$	8.04

^{a} eV.

the $^1(\pi \rightarrow \pi^*)$ transition in this type of molecules. Such a refinement consists in supplementing the hole-particle description by adding a second hole-particle couple: both couples are determined at the same time ["two configuration electron hole potential" (TCEHP) method]. In our opinion such a method should be used with some caution because it is possible that a straightforward application gives a state with a larger component in the $(n \rightarrow \sigma^*)$ excitation. In Table IV we report the results obtained for methylenimine by adopting different choices of the second hole-particle couple.

Both EHP and TCEHP methods give approximations to the results one can obtain by performing a complete CI over all the single excitation configurations (CSECI method). In Table V we report the CSECI results for methylenimine. By comparing the results of Tables III and V it turns out that EHP gives good approximations for all states with the exception of the $^1(\pi \rightarrow \pi^*)$ one which is better represented in the TCEHP method. On the other hand, it can be remarked that double excitations are supposed to contribute significantly in describing this state in small molecules such as ethylene[11] and formaldehyde[12] and that the results heavily depend on the basis set: Del Bene et al.[13] infer that single excitation CI gives transition energies up to 3 eV too high for minimal basis set calculations and up to 1.5 eV too high for split valence shell basis (4-31G) calculations.

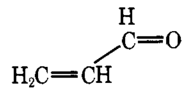
The $(\pi \rightarrow \pi^*)$ band in the alkyl azomethines is asymmetric, with possible shoulders at longer wavelengths.[14] Such transitions are attributed to a weaker Rydberg transition $^1(n \rightarrow 3s)$ or to a $^1(n \rightarrow \sigma^*)$ excitation.[2] Incidentally, we remark that in the range of energies under examination there also appears a $(\pi \rightarrow \sigma^*)$ transition with an oscillator strength eight times greater than for the $(n \rightarrow \sigma^*)$ transition.

The minimal basis set calculations give an acceptable value for the lowest transition, but the results worsen progressively when one goes to higher excitations. The virtual orbital manifold is too much restricted in this basis set to get sensible approximations to high energy transitions.

When the azomethine group is conjugated to a phenyl ring, the absorptions due to the weak C=N chromophore are submerged by strong absorptions due to $\pi \rightarrow \pi^*$ transitions of the aromatic moiety.[15] It is well known that a minimal basis set is not adequate to describe the UV spectrum of benzene because of the high symmetry of this molecule. In the two molecules here considered, the symmetry lowering can be regarded only as a perturbation to a local high symmetry, and the considerations on the inadequacy of the minimal basis set to describe local excitations in the ring maintain their validity. Our results on the contrary emphasize the transitions involving the azomethine chromophore.

There is a general agreement among the spectroscopists[14,15] that the only transition due to an internal excitation of the azomethine group is, in both molecules, the $^1(n \rightarrow \pi^*)$ one, which might be hidden under the strong $\pi \rightarrow \pi^*$ band corresponding to a locally excited benzene state. It should be remarked that according to the present calculations, the conjugation with a phenyl ring produces a shift of this band to lower wavelengths. This fact is in contrast with the intuitive considerations generally accepted for similar compounds.[16] The main reason for this behavior is due to the energy shift of the lowest π^* orbital in passing from $H_2C{=}NH$ to molecules **1** and **2** (see Table I).

It can be helpful to compare our results with those pertinent to the simpler conjugated compounds *trans*-acrolein (**4**) and its iminic derivative **5**, where one can ascertain that there are two reasons for such behavior, both related to the basis set. The first would seem specific to the STO-3G + p basis set: in the *trans*-acrolein molecule, Iwata and Morokuma[14] found a blue shift of 0.11 eV with respect to the isolated formaldehyde molecule, whereas with the STO-3G and 4-31G basis sets, a correct trend was observed. Analogously for molecule **5** we get a 0.11 eV blue shift with respect to the methylenimine molecule in the STO-3G + sp basis and an opposite trend in the other two bases.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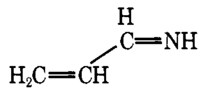
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The second reason is related to the use in the present case of a minimal basis set for the aromatic moiety of our molecules. Referring again to molecule **5** we observe that, by adopting a minimal basis set on the C=C moiety of the molecule and a STO-3G + sp one on the C=N portion, a 0.56 eV blue shift is obtained. It is our impression, we would add in passing, that red shifts of the azomethine chromophore due to conjugation in $n \rightarrow \pi^*$ excited states should be smaller than in the corresponding carbonyl compounds.

In molecules **1** and **2**, the $^1(\pi \rightarrow \pi^*)$ transitions are overestimated for the same reasons reported in the discussion on the methylenimine molecule. Assuming that in the present case again there is an error of about 20%, the corrected transition energies fall in the range of observed transitions in Ph-$CH{=}NCH_3$[3,18] and Ph-$N{=}CHC_2H_5$.[3] The mixing with $(\sigma \rightarrow \sigma^*)$ configurations introduced by the TCEHP method produces a lowering in the transition energy of less than 0.3 eV.

The EHP wave functions, if compared with those obtained by simple virtual orbital substitution, have a neater localized character (especially with the STO-3G + sp basis set), i.e., the mixing of canonical occupied MO's and the mixing of virtual orbitals to create the hole and the particle reinforce the partial localization already present in the original canonical MO set. The $^1(n \rightarrow \pi^*)$ state corresponds, in both molecules, to a local excitation on the azomethine group. The $^1(\pi \rightarrow \pi^*)$ state has a charge transfer character, with electronic charge passing from the ring to an antibonding orbital having a dominant contribution on the C=N- group. The $^1(\pi \rightarrow \sigma^*)$ state again corresponds to a charge transfer state, with electron transfer from the ring to a σ^* orbital localized on the azomethine group.

The general features of the triplet states are similar to those of the corresponding singlets, the most noticeable deviations being in the couple of $^{1,3}(\pi \rightarrow \pi^*)$ states to which we will return later.

Table VI. Population Analysis and Dipole Moments (STO-3G + sp Basis) for Benzaldimine (**1**) and *N*-Phenylformaldimine (**2**)

Group		Ground	$^1(n \rightarrow \pi^*)$	$^3(n \rightarrow \pi^*)$	$^1(\pi \rightarrow \pi^*)$	$^3(\pi \rightarrow \pi^*)$	$^1(\pi \rightarrow \sigma^*)$	$^3(\pi \rightarrow \sigma^*)$
					Molecule **1**			
CH	σ	6.219	6.103	6.124	6.219	6.219	7.874	7.855
	π	0.905	1.411	1.411	1.329	1.004	0.854	0.845
NH	σ	6.743	5.904	5.878	6.742	6.742	6.085	6.104
	π	1.272	1.608	1.623	1.354	1.318	0.934	0.902
C_6H_5	σ	35.039	34.992	34.998	35.039	35.039	35.042	35.041
	π	5.822	5.981	5.966	5.317	5.677	5.212	5.253
μ_x[a]		0.23	1.25	0.92	−5.60	−0.99	−10.85	−10.19
μ_z		−2.71	1.61	1.69	−5.55	−4.01	−8.21	−8.10
μ_{tot}		2.72	2.04	1.92	7.88	4.13	13.61	13.02
					Molecule **2**			
CH_2	σ	7.249	7.098	7.120	7.249	7.249	8.295	8.278
	π	0.915	1.519	1.501	1.474	1.060	0.675	0.664
N	σ	5.822	5.069	5.023	5.822	5.822	5.759	5.776
	π	1.151	1.474	1.514	1.209	1.133	1.035	1.026
C_6H_5	σ	34.929	34.834	34.858	34.929	34.929	34.946	34.946
	π	5.934	6.008	5.985	5.317	5.807	5.290	5.310
μ_x		−2.86	−1.97	−1.88	−9.13	−4.01	−7.39	−7.35
μ_z		0.45	−2.61	−2.80	−7.30	−1.38	−14.21	−14.32
μ_{tot}		2.90	3.27	3.38	11.69	4.24	16.02	16.09

[a] The *z* axis points along the azomethine group in the direction opposite to the Ph ring. The *x* axis lies on the molecular plane pointing in the direction opposite to the Ph ring. The dipole moments are given in debyes.

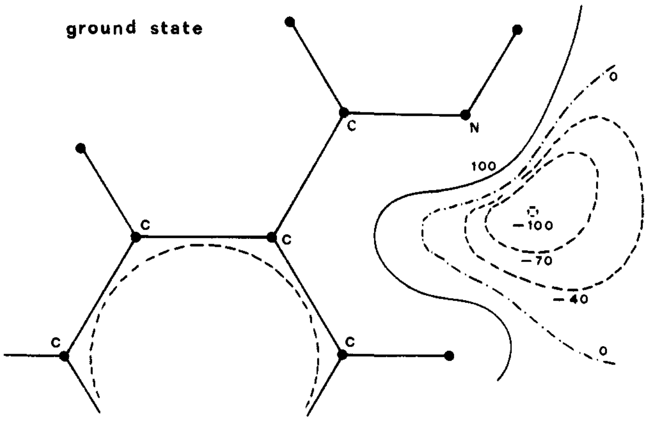

Figure 1. Electrostatic potential (kcal/mol) in the molecular plane of benzaldimine (**1**). Ground state.

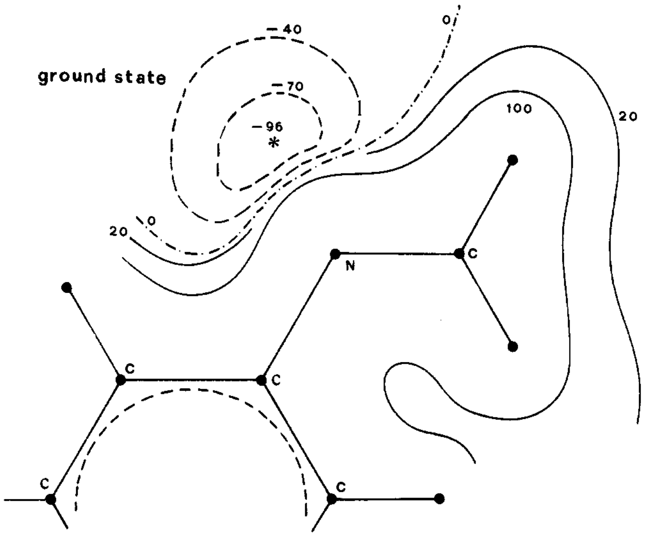

Figure 2. Electrostatic potential (kcal/mol) in the molecular plane of *N*-phenylformaldimine (**2**). Ground state.

An appraisal of the inner charge transfer effects can be obtained by means of the population analysis data reported in Table VI. In the $^1(n \rightarrow \pi^*)$ state of molecule **1**, there is a net loss of 0.11 electrons in the azomethine group, a charge transfer due to a compensation between a loss of 0.95 σ electrons, and a gain of 0.84 π electrons. In the same state of molecule **2**, the final balance gives a gain of 0.02 electrons for the $-N{=}CH_2$ group. In both molecules a large rearrangement of the charge distribution produces only small net charge shifts between the two portions of the molecule.

Further information on the electronic distribution in a given electronic state ν may be obtained by analyzing the electrostatic potential function $V_\nu(\vec{r})$ for the state under examination. $V_\nu(\vec{r})$ is directly linked to the charge distribution:

$$V_\nu(\vec{r}) = -\int \frac{\rho_\nu(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d\vec{r}_1 + \sum_\alpha \frac{Z_\alpha}{|\vec{r} - \vec{R}_\alpha|}$$

and $V_\nu(\vec{r})$ maps are able to give a deeper insight into the charge distribution itself than $\rho_\nu(\vec{r})$ maps directly do. The amount of information one gets in this way is perhaps comparable with that obtainable by means of $\Delta\rho(\vec{r})$ maps (density difference between two different molecular states or between ρ_ν and the density distributions of the isolated atoms), but V_ν gives, in addition, some information on the molecular reactivity. For this subject the reader is referred to preceding papers.[19] It may be remarked that, for vertical excitation states, the information on chemical reactivity one may derive from V_ν does not include the effect of relaxation processes to more stable geometries, which are more rapid than collisions with reacting molecules.

Figures 1 and 2 report for molecules **1** and **2**, respectively, maps of V_g (g stands here for ground state) in a portion of the molecular plane. The interpretation of the shape of V_g is clear in both molecules and analogous to that found in other cases: there is a unique negative region corresponding to the N lone pair.[20] The value of the minimum represents the electrostatic part of the proton affinity of the group which results decidedly higher in molecule **1**. (The minima are −103 kcal/mol for **1** and −96 kcal/mol for **2**.

The $V_{n \rightarrow \pi}$ maps (see Figures 3 and 4) clearly show the dis-

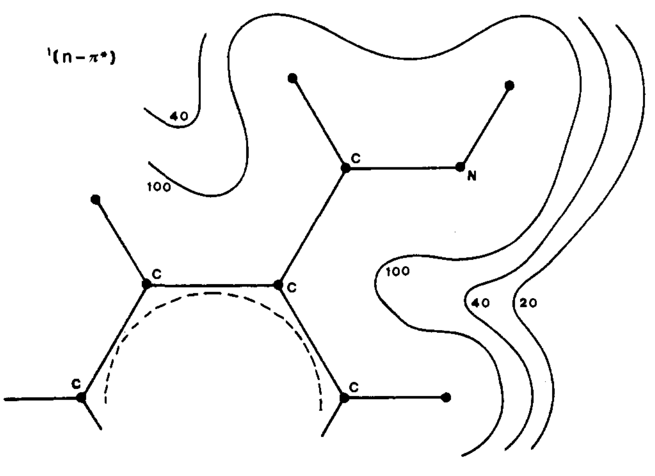

Figure 3. Electrostatic potential in the ¹(n → π*) state of **1**.

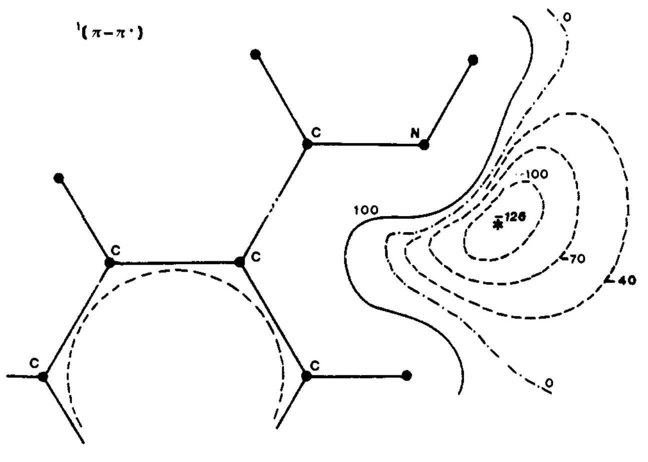

Figure 5. Electrostatic potential in the ¹(π → π*) state of **1**.

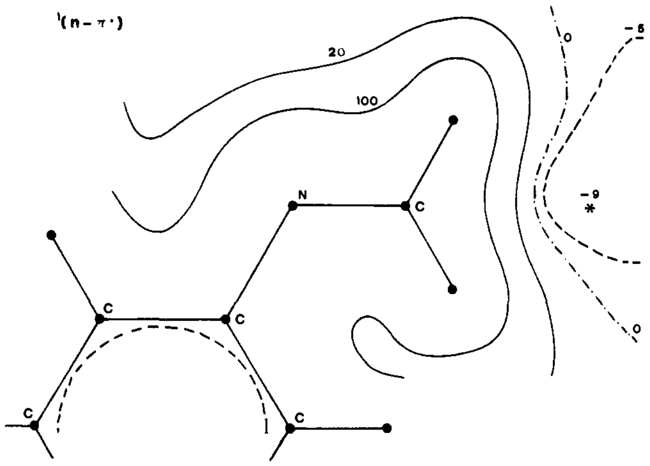

Figure 4. Electrostatic potential in the ¹(n → π*) state of **2**.

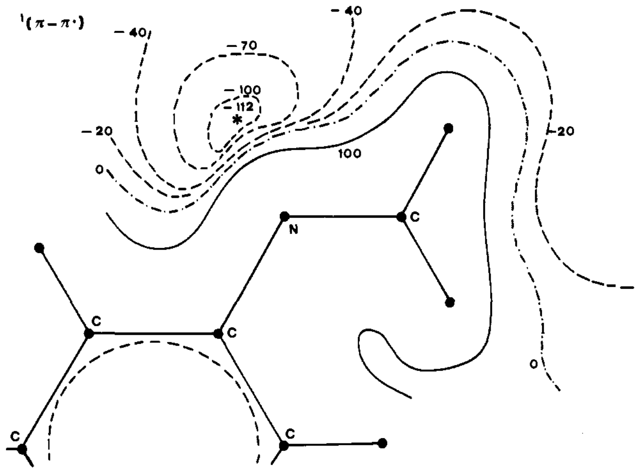

Figure 6. Electrostatic potential in the ¹(π → π*) state of **2**.

appearance of an electron on the lone pair: the negative region facing the N atom is completely deleted, while in the orthogonal plane containing the C–N bond, $V_{n\to\pi^*}$ shows a noticeable enlargement of an already existing negative region, due to the π electrons of the C=N bond. (For the sake of brevity, the corresponding maps are not reported here.) In molecule **2**, such negative region reaches the molecular plane (see Figure 4). It must be remarked that the proton affinity appears to be, in the electrostatic approximation, decidedly lower in the ¹(n → π*) state than in the ground one for both molecules.

In the ¹(π → π*) state of molecule **1** there is a gain of 0.50 electrons on the azomethine group, the largest part of which concerns the C atom. In molecule **2** the electron gain of the C=N group is comparable (0.62 electrons), and in this case, again, the largest part concerns the C atom. An inspection of the dipole moments (Table VI) leads to the same conclusion. In both molecules a large charge shift is evident ($\Delta\mu$ = 1.4 for **1** and 8.8 for **2**), and the variation of μ is larger in **2** than in **1** because in **2** the C atom is farther from the ring than in **1**.

The $V_{\pi\to\pi}$ maps for molecules **1** and **2** are reported in Figures 5 and 6, respectively. In this case, again, we report a map on the molecular plane because the minimum lies in this plane. The general shape of the $V_{\pi\to\pi^*}$ maps are similar to those of V_g, but the changes in this plane are remarkable, although the σ electron distribution remains unchanged with respect to the ground state. The enlargement of the negative regions and the deepening of the potential energy holes (evident in both molecules) correspond to an increase of nucleophilicity passing from the ground state to the ¹(π → π*) one. It can be remarked that the difference in nucleophilic character between **1** and **2** is larger in this excited state.

In the region outside the molecular plane there are changes in V which correspond to the transfer of 0.5–0.6 π electrons, i.e., there is a noticeable reduction of the negative region corresponding to the π electrons of the ring and a corresponding increase in the π region of the C=N bond.

As remarked above, the largest difference between singlet and triplet states occurs for the π → π* excitation. The charge shift to the azomethine is decidedly lower in the triplet state (0.14 electrons for **1** and 0.13 electrons for **2**). Accordingly, the V maps show smaller variations with respect to the ground state than those displayed in Figures 5 and 6 for the ¹(π → π*) states. The minima of $V_{\pi\to\pi^*}$ for the triplet case are −112 kcal/mol (**1**) and −96 kcal/mol (**2**).

In the (π → σ*) state, there is a gain of 0.61 electrons for the azomethine group in molecule **1** and of 0.63 electrons in molecule **2**. Such net gains are derived from a compensation of different effects on the C and N portions of the azomethine group. In fact, in molecule **1** there is a gain of 1.60 electrons on =CH– and a loss of 1.00 electrons on =NH, while in molecule **2** there are lower gains on CH_2 (0.81 electrons) and lower losses on =N– (0.18 electrons). The differences between the dipole moments of the two molecules are completely understandable if one takes into account the different spatial locations of the atoms.

The $V_{\pi\to\sigma^*}$ maps on the molecular plane (Figures 7 and 8) evidence the fact that the σ* particle has a large component on the C atom of the azomethine group. The nucleophilicity

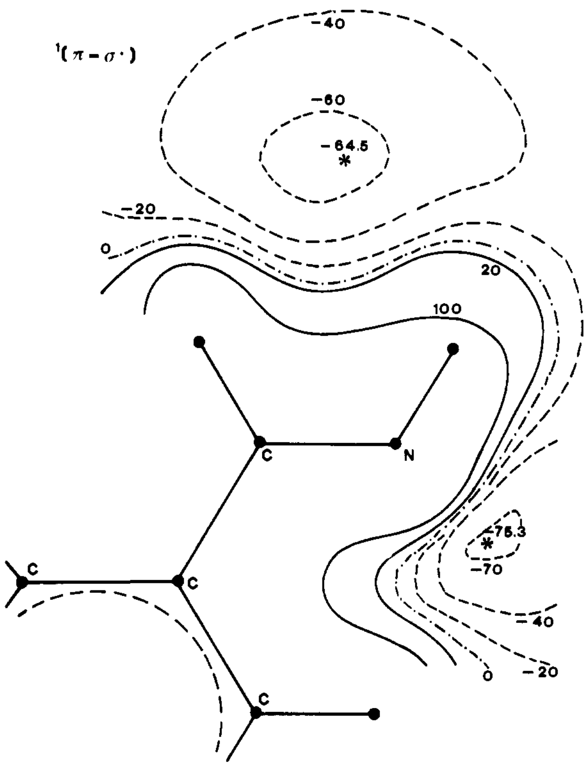

Figure 7. Electrostatic potential in the $^1(\pi \rightarrow \sigma^*)$ state of **1**.

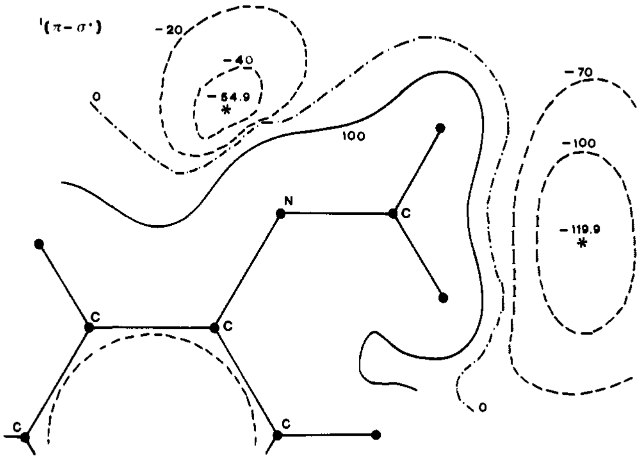

Figure 8. Electrostatic potential in the $^1(\pi \rightarrow \sigma^*)$ state of **2**.

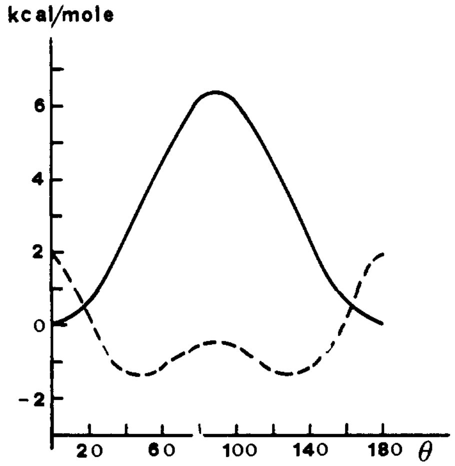

Figure 9. Torsional energy for the ground state of benzaldimine (full line) and *N*-phenylformaldimine (dashed line) in the STO-3G basis. The coplanar structure corresponds to $\theta = 0°$.

of the N atom somewhat decreases in both molecules (the corresponding minima of $V_{\pi\rightarrow\sigma^*}$ are −75 kcal/mol in **1** and −55 kcal/mol in **2**), and a second negative region facing the C atom appears. In **2** this second region contains the absolute minimum of V (−119 kcal/mol). The occurrence of negative regions of V in correspondence to hydrocarbon portions of a molecule has already been evidenced and interpreted in ground state molecules.[21,22]

Concluding Remarks

In the present description of the three lowest excited states of benzaldimine and *N*-phenylformaldimine, there is no evidence for dramatic changes in the electron donor/acceptor properties of the azomethine group when linked to a phenyl group at its C or N end. There is however, a hint that constantly the electron acceptor properties of the C=N– group, measured by the charge transfers in the excited states, are larger when the ring is attached to the nitrogen (molecule **2**). These conclusions have been reached by analyzing the population data and the shape of the electrostatic molecular potential V.

V gives, in addition, some information about the chemical reactivity of the various electronic states. A larger affinity toward positively charged reactants in **1** with respect to **2** was found in the ground, $^1(n \rightarrow \pi^*)$, and $^1(\pi \rightarrow \pi^*)$ states (and in the corresponing triplets also), while in the $^1(\pi \rightarrow \sigma^*)$ state the situation is less clear. It should be remembered that such information concerns states having the same geometry as the ground one and does not include the effect of the relaxation of the geometry.

A subject which deserves some remarks is the reliability of the results presented in this paper. Three possible sources of error can be considered: method, basis set, and molecular geometry adopted in the calculations.

It is, at present, sufficiently well known how the EHP method works for molecules containing X=Y chromophores. It gives a good approximation to the complete CI based on single excited configurations (CSECI),[4,17] sufficient to represent $^{1,3}(n \rightarrow \pi^*)$ and $^3(\pi \rightarrow \pi^*)$ states. Worse is the representation this method gives for the $^1(\pi \rightarrow \pi^*)$ state, and the approximation is only partially improved when one passes to the TCEHP method (which gives a still better approximation to CSECI) because double excitations are supposed to be essential to a good description of this state. There is, in fact, the possibility that the inclusion of doubly excited configurations, which are not considered either in the CSECI method or in their approximations EHP and TCEHP, should produce substantial changes in the description of the electronic distribution of the excited states. About this topic, we can anticipate some results of a comparison of the description of V given by the EHP method and an extended CI treatment for the $^1(\pi \rightarrow \pi^*)$ state of $H_2C{=}O$ (calculations on a STO-3G + p basis set performed in collaboration with H. Le Rouzo, CMOA, Paris): the inclusion of the 616 most important configurations shrinks the negative region on the vertical of the CH_2 group (the minimum of V passes from −18 kcal/mol in the EHP description to −6 kcal/mol in the CI one) and at the same time increases the importance of the negative contributions to V in the region of the O lone pairs. In other words, the inclusion of doubly excited configurations brings to rearrangements of the electronic charge distribution of the $^1(\pi \rightarrow \pi^*)$ state, including also some contraction.

On the other hand, such effects due to an improvement in the description of the excited state run almost parallel in other molecules containing the X=Y chromophore, and consequently there are good reasons to believe that the conclusions of the present paper, which is concerned with comparisons between molecules treated at the same level of accuracy, do not change drastically if a more complete CI treatment should be performed.

The ($\pi \rightarrow \sigma^*$) states have not deserved thus far much attention, and the information about the ability of the EHP method to describe this state is scarce.

In the preceding discussion we have employed the results obtained with a basis set having diffuse functions only on the azomethine atoms. The unbalance of this basis set might introduce some distorsions in the electronic density distribution. We have performed as a control parallel calculations with the minimal basis set STO-3G (calculations on molecules of this size with diffuse orbitals on all the atoms go beyond our possibilities). We found that both basis sets lead practically to the same conclusions in regard to the entity of the charge transfers and to the main features of V, in spite of the already remarked difference in the extension of the π^* orbital in the two basis sets. The only exception concerns the ($\pi \rightarrow \sigma^*$) states which are not related in the two basis sets. Of course, if one passes to larger basis sets, different charge transfers and different shapes for V will be found, but the basis set here adopted seems to be sufficient for comparing changes in the electron distribution on the C=N- group in related molecules because the ring acts as a sort of perturbator able to give or to receive electrons. Unpublished calculations on smaller compounds having a X=Y chromophore conjugated to a vinyl group indicate that an enlargement of the basis set produces a small lowering in the charge transfer. In any case we have never observed a reversal of the charge flow, and consequently we are induced to consider the *comparisons* among charge displacements of related molecules reported in this paper, as sufficiently representative of the actual phenomena occurring in **1** and **2** after vertical excitation.

The experimental geometry of **1** and **2** is not known, and we have adopted an idealized planar geometry with distances averaged on x ray findings on related compounds. The main source of error in our comparisons could be done by the occurrence in the ground state of a rotation around the bond connecting the two groups and leading to a noncoplanar structure. There are experimental results which suggest this possibility in **2** and discard it in **1**.[24] We report in Figure 9 the rotational profile for the ground state in the SCF approximation: the structure of **1** is coplanar whereas for **2** the planar structure corresponds to a maximum. The energy curve is, however, decidedly flat, and at room temperature the molecule can assume all the rotational conformations. A description of the energy shifts in excited states as a function of the rotation of the groups would bring about additional problems, both methodological and computational to be taken up in a separate investigation.

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(7) To give an idea of the different spatial extension of the 2b and 8a virtual orbitals of CH_2NH in the two basis sets, we report here their $\langle y^2 \rangle$ values in a.u. where y is the axis perpendicular to the molecular plane; $\langle y^2 \rangle_{2b} =$ 1.231 (STO-3G) and 9.201 (STO-3G + sp); $\langle y^2 \rangle_{8a} = 0.497$ (STO-3G) and 8.452 (STO-3G + sp). We do not want to discuss here the subject concerning the correct definition of Rydberg orbitals. To this purpose we might refer the reader, for instance, to the paper of H. Basch and V. McKoy [*J. Chem. Phys.*, **53**, 1628 (1970)], where, among other things, much higher values of $\langle y^2 \rangle$ are reported for the Rydberg orbitals of the ethylene molecule.

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