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Nature of Nonbonding Molecular Orbitals: Application to Two Symmetric Tetraazanaphthalenes

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The “nonbonding” or n-orbitals of two tetraazanaphthalenes cannot be satisfactorily analyzed using the conventional model of through-space and through-bond interactions between nitrogen lone pairs, as this approach does not adequately explain the energy ordering of the n-orbitals in molecules such as 1,4,5,8-tetraazanaphthalene and 2,3,6,7-tetraazanaphthalene. An alternative computational approach is presented, in which the electronic structure of these molecules is viewed as arising from substitution-induced perturbations to the parent molecule, naphthalene. Semiempirical calculations at the CNDO/S level show that the n-orbitals can be understood in terms of perturbed naphthalene-like σ-orbitals, often with significant contributions from σ^*-orbitals. This approach has been found to be instructive and quantitative, with potential applications to a wide range of related molecules.

I. Introduction

Lone pairs are a characteristic feature of heterocyclic molecules and have profound effects on their chemical and physical properties. For example, they strongly affect the electronic absorption and emission spectra of many compounds, and the detailed analysis of these spectra typically requires knowledge of the energies and properties of one or more (π^*, n) states.[1] This paper investigates the “nonbonding” or n-orbitals that constitute the lone pairs in two symmetric tetraazanaphthalenes and demonstrates a computational approach that could profitably be used on a much wider range of heterocyclic compounds.

A heterocycle that contains two or more nitrogen atoms will have two or more lone pairs that can, in principle, interact with each other and with other orbitals in the molecule. Earlier studies of these interactions have raised important questions about how the interactions manifest themselves in the electronic spectra of these molecules and the extent to which lone-pair electrons remain localized on the nitrogen atoms.[2,3] A related question is the extent to which the heterocycle is aromatic, given the tendency of the nitrogens to localize charge at the expense of the delocalized π electrons. A number of different approaches have been used to study the interactions between lone-pair orbitals. The most common school of thought is that in the first instance there is a direct or “through-space” interaction between the orbitals, leading to the formation of two or more n-type molecular orbitals (MOs).[2,4] There are also “through-bond” interactions between these MOs and the σ-bonding framework of the molecule; these interactions are believed to occur only between orbitals that have the same symmetry and similar energies. The result of these two types of interactions is an energy splitting of the n-type MOs. The splitting reflects the magnitudes of the two types of interaction, and the balance between them, since through-bond interactions may augment, reduce, or even reverse the through-space splittings. Through-bond interactions, which involve mixing between n- and σ-orbitals, may introduce some bonding character into the lone pairs, and thus they may not be exclusively nonbonding orbitals. Interactions involving n-MOs become increasingly complicated and difficult to study in molecules with more than two nitrogens, and indeed our experimental and computational studies of the electronic spectra and structures of 1,4,5,8-tetraazanaphthalene (1458-TAN; see Figure 1 for the numbering scheme) and 2,3,6,7-tetraazanaphthalene (2367-TAN) reveal that earlier approaches to rationalizing the formation of n-orbitals is too simple and a more consistent and quantitative approach is required.

The tetraazanaphthalenes are of particular theoretical interest as they contain four nitrogen atoms substituted into a naphthalene framework in a range of different patterns. The 13 different arrangements possible for these four nitrogen atoms, with two heteroatoms in each ring, lead to a variety of possible interactions of the nitrogenic n-orbitals and provide an excellent opportunity for systematically studying these interactions. In particular, the n-MOs of 1458-TAN have long been recognized as an important test case.[2] Even though this molecule and 2367-TAN both belong to the D_{2h} point group, they are expected to have very different patterns of splitting for their four n-MOs.[2] In the case of 2367-TAN, there are two pairs of adjacent nitrogens which should interact strongly through space owing to the extensive overlap of their orbitals; there would, however, be virtually no through-space interaction between the nitrogens in the 2 and 7, or 3 and 6 positions (see Figure 1). For 1458-TAN, the only significant through-space interaction would be between the lone-pair orbitals located on the nitrogen atoms in the 1 and 8 positions, and the 4 and 5 positions. The separation of the nitrogen atoms in the 1 and 4 positions is too great for any appreciable overlap to occur, and in any case, the lone-pair orbitals point in opposite directions. For both molecules, there will also be significant through-bond interactions, and indeed for 1458-TAN these interactions are predicted to give a large and distinctive splitting of the n-type MOs.[2] These predictions

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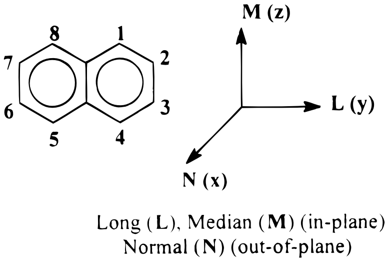


Figure 1. Molecular numbering and axis labels.

TABLE 1: CNDO/S-CI Calculations for the Excited Electronic States of 1458-TAN

wavelength (nm)	wavenumber (cm^{-1})	symmetry	polarization	transition type	f^a
434.7	23003	B_{1g}	*b*	$\pi^* \leftarrow n$	
356.1	28081	B_{3u}	N	$\pi^* \leftarrow n$	0.014
308.1	32456	B_{2u}	L	$\pi^* \leftarrow \pi$	0.386
272.0	36760	B_{2g}	*b*	$\pi^* \leftarrow n$	
267.0	37451	A_u	*b*	$\pi^* \leftarrow n$	
256.9	38923	B_{2g}	*b*	$\pi^* \leftarrow n$	
233.6	42817	B_{1u}	M	$\pi^* \leftarrow \pi$	0.005
230.2	43433	A_g	*b*	$\pi^* \leftarrow \pi$	
206.1	48528	B_{1u}	M	$\pi^* \leftarrow \pi$	0.752
199.9	50019	B_{3u}	N	$\pi^* \leftarrow n$	0.0002
192.6	51914	A_u	*b*	$\pi^* \leftarrow n$	
191.2	52289	B_{2g}	*b*	$\pi^* \leftarrow \pi$	
188.6	53013	B_{2u}	L	$\pi^* \leftarrow \pi$	1.410

[a] f = predicted oscillator strength of the transition. [b] Denotes a forbidden transition.

TABLE 2: CNDO/S-CI Calculations for the Excited Electronic States of 2367-TAN

wavelength (nm)	wavenumber (cm^{-1})	symmetry	polarization	transition type	f^a
344.0	29050	B_{1g}	*b*	$\pi^* \leftarrow n$	
314.5	31799	B_{2g}	*b*	$\pi^* \leftarrow n$	
310.7	32186	B_{3u}	N	$\pi^* \leftarrow n$	0.024
280.5	35646	A_u	*b*	$\pi^* \leftarrow n$	
266.1	37579	B_{2u}	L	$\pi^* \leftarrow \pi$	0.120
237.5	42107	B_{2g}	*b*	$\pi^* \leftarrow n$	
232.3	43041	B_{1u}	M	$\pi^* \leftarrow \pi$	0.124
222.4	44965	B_{1g}	*b*	$\pi^* \leftarrow n$	
209.1	47835	A_u	*b*	$\pi^* \leftarrow n$	
203.1	49245	A_g	*b*	$\pi^* \leftarrow \pi$	
200.4	49889	B_{3u}	M	$\pi^* \leftarrow \pi$	0.0001
196.1	51008	B_{2u}	L	$\pi^* \leftarrow n$	1.53
192.1	52058	B_{1u}	M	$\pi^* \leftarrow \pi$	0.733

[a] f = predicted oscillator strength of the transition. [b] Denotes a forbidden transition.

are supported by experimental UV−visible spectra, but as shown below, this simple dissection of n-orbital interactions into through-space and through-bond components is on the whole both difficult and unsatisfactory. A more systematic and quantitative approach is proposed, using semiempirical MO calculations in the first instance.

MO calculations are used extensively for characterizing the ground and excited electronic states of molecules, as well as their normal vibrational modes. Ab initio and semiempirical SCF programs have been used to predict transition energies, band intensities, oscillator strengths, and band polarizations for $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions.[5] Semiempirical calculations using the CNDO methodology with configuration interaction (CNDO/S-CI) are fairly reliable for small to medium-sized molecules,[6,7] and we are currently testing their applicability to larger and more complex molecules such as the tetraazanaphthalenes, including 1458-TAN, 2367-TAN, and 1358-TAN (pteridine).[8] In molecules with adjacent nitrogen atoms, such as 1,2,3-triazine,[9] semiempirical predictions have not been so reliable. This may also be the case for 2367-TAN, but the limited experimental results that are available do not allow us to see how accurate the calculations are for this system.[10] However, good results for 1458-TAN have encouraged us to persist with this approach and extend the CNDO study to the n-orbitals that are involved in the $\pi^* \leftarrow n$ transitions of these molecules.

The CNDO method works within the LCAO approximation, and the calculated MOs for a molecule may be expressed as linear combinations of atomic orbitals. As shown below, this permits a detailed analysis of the n-type MOs in a particular tetraazanaphthalene. Quantitative comparisons with the σ-type orbitals of naphthalene are possible, giving improved understanding of the nature of the n-orbitals, particularly in more highly substituted molecules.

II. Methods

CNDO/S-CI calculations were carried out on 1458-TAN, 2367-TAN, and the parent molecule, naphthalene, using a modified version of the standard QCPE program.[11] Optimized input geometries were calculated at the HF/6-31G* level using the Gaussian family of programs.[12]

Experimental details of the electronic spectrum of 1458-TAN will be published separately.[8] Transition energies for 2367-TAN were obtained from the literature spectrum of Adembri et al.[10]

III. Results and Discussion

Tables 1 and 2 summarize the results of the CNDO/S-CI calculations for 1458-TAN and 2367-TAN, respectively. The polarization directions for the molecules are shown in Figure 1. Figures 2 and 3 compare the calculated and experimental transition energies for 1458-TAN and 2367-TAN, respectively. For 1458-TAN, there is good agreement between theory and experiment for the lowest energy $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions.[8] The predicted second $\pi^* \leftarrow n$ transition, which is attributed to a B_{3u} (π^*, n) excited state, is unfortunately not seen in the experimental spectrum. It has presumably been swamped by the neighboring and strongly allowed $\pi^* \leftarrow \pi$ (B_{2u}) transition. Ab initio calculations at the CIS/3-21G level confirm the CNDO/S-CI predictions for the ordering of the two lowest $\pi^* \leftarrow n$ transitions[13] and give a good prediction of the transition energy. The CIS calculations also make valuable predictions of the excited-state vibrational frequencies of this compound, and details will be published separately, together with a full analysis of the 1458-TAN spectrum.[8] The experimental data for 2367-TAN are sparse, but there appears to be a reasonably good fit between theory and experiment for the lowest energy $\pi^* \leftarrow n$ transition. We conclude that, for the lower energy transitions, the CNDO/S-CI method performs well, and this supports its further use for studying the n-orbitals of these molecules. In the following subsections, we show how a simple analysis of the n-orbitals in terms of through-space and through-bond interactions is unsatisfactory and then demonstrate a better computational approach.

Interactions between n-Orbitals. When a molecule contains more than one nitrogen atom, the proximity and relative orientation of the lone-pair or n-orbitals greatly influences the energy splittings of the resulting MOs as a result of the through-space and through-bond interactions. When the greatest effect felt by one n-orbital, n_1, is the close proximity of another, n_2, then this through-space coupling has a stabilizing effect on the symmetric ($n_1 + n_2$) combination and a destabilizing effect on the antisymmetric ($n_1 - n_2$) combination[4,14] making the symmetric combination lie at a lower energy than the antisymmetric.

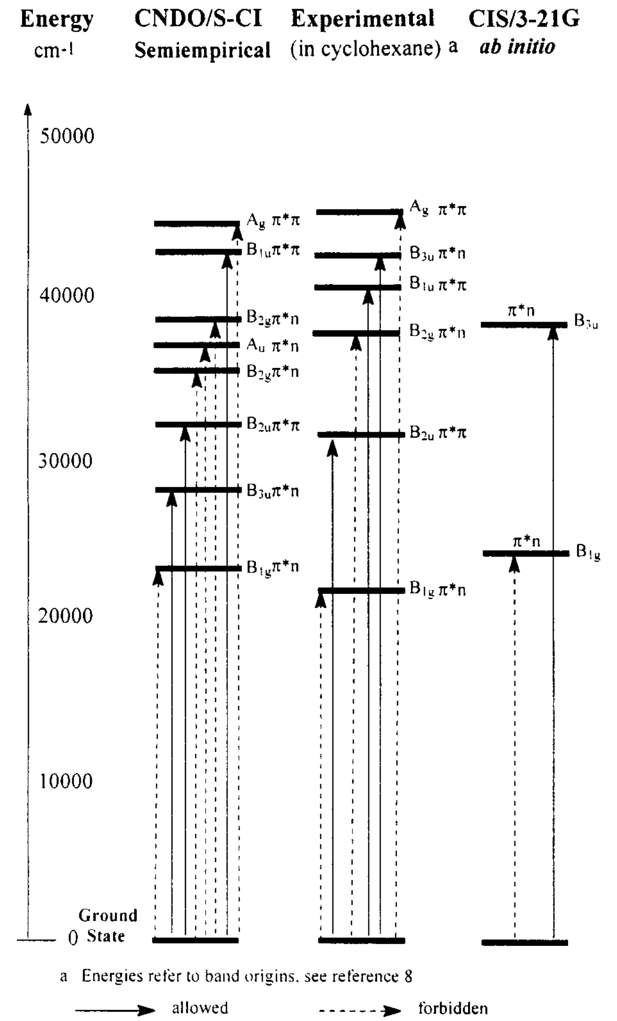


Figure 2. Energy level diagram for 1458-TAN.

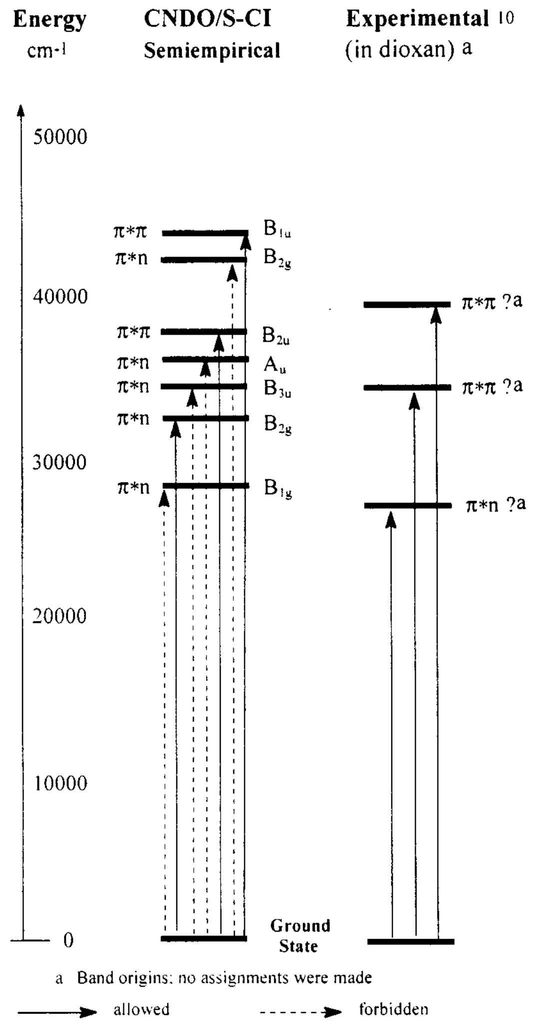


Figure 3. Energy level diagram for 2367-TAN.

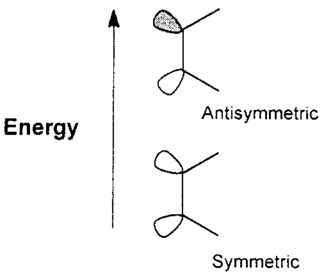


Figure 4. Ordering of adjacent n-molecular orbital combinations (sign of the wavefunction: unshaded +ve, shaded −ve).

The direct or through-space interaction of the n-orbitals is a short-range effect and is therefore less significant for 1458-TAN. In 2367-TAN, there should be strong through-space coupling between the orbitals on the adjacent nitrogens, placing the symmetric combinations at lower energy (see Figure 4).

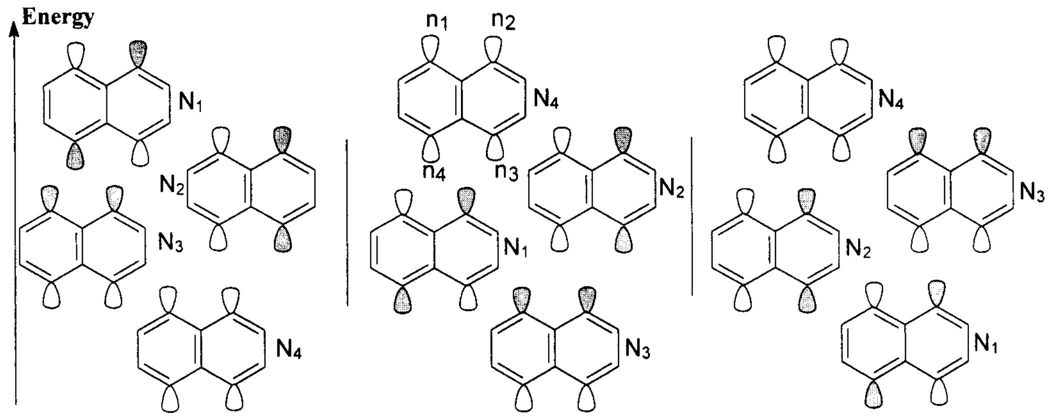
In the tetraazanaphthalenes, the four n-orbitals combine in four different ways. The resulting combinations for the most symmetric molecules (D_{2h} point group) are as follows:

$$\begin{array}{ll} N_1 = n_1 - n_2 + n_3 - n_4 & [b_{3g}] \\ N_2 = n_1 - n_2 - n_3 + n_4 & [b_{2u}] \\ N_3 = n_1 + n_2 - n_3 - n_4 & [b_{1u}] \\ N_4 = n_1 + n_2 + n_3 + n_4 & [a_g] \end{array}$$

where n_1, n_2, n_3, and n_4 represent the original individual n-orbitals located on each of the nitrogen atoms. The resulting n-MO combinations (N_1, N_2, N_3, and N_4) therefore have different energies and symmetries (see above).

n-Orbitals of 1458-TAN. When only through-space interactions are taken into account, the n-type MOs of 1458-TAN should be ordered as illustrated in Figure 5a, but possibly interleaved with the higher energy σ-orbitals. For simplicity, we will consider only the n-orbitals at present. The wave functions for the N_2 and N_3 combinations have only one nodal plane, and at first sight these MOs may appear to be degenerate. However, N_3 should have stronger bonding-type overlaps (involving the nitrogens in the 1 and 8, and 4 and 5 positions) than N_2 and therefore should lie at slightly lower energy. The CNDO/S-CI calculations, which take both through-space and through-bond interactions into consideration, predict a different orbital ordering, as illustrated in Figure 5b. The photoelectron study by Gleiter et al.[15] assigns the four highest energy n-orbitals in the same order as our CNDO/S-CI calculations.

The results that are summarized in Figure 5b are consistent with the suggestion that through-bond interactions of the n_1 and n_2 orbitals (and similarly n_3 and n_4) have a destabilizing effect on the N_4 combination, as predicted by the semiempirical calculations of Hoffmann.[4] There are also predicted to be substantial interactions between n_1 and n_4, as well as n_2 and n_3, as seen in quinoxaline.[2,16] If Hoffmann's prediction of the strength of through-bond and through-space interactions is taken



(a) Through space interaction only (b) CNDO/S-CI calculation (c) Based on Hoffmann's prediction

Figure 5. Ordering of n-molecular orbital combinations for 1458-TAN.

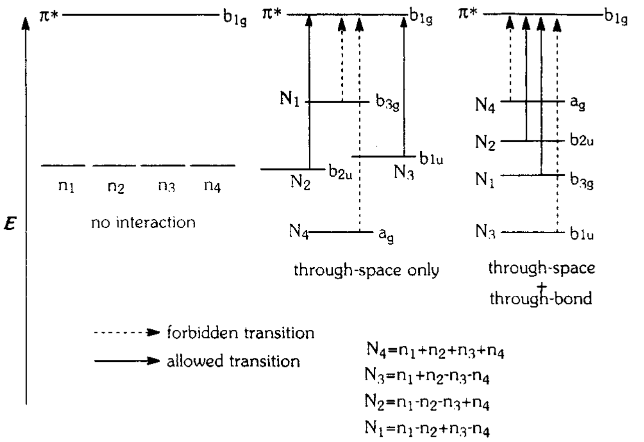


Figure 6. Energy level diagrams for 1458-TAN (not to scale) (ordering based on CNDO/S-CI calculations).

further, the ordering then differs from our calculated results (see Figure 5c). Hoffmann's predictions, however, may also be an oversimplification in the case of the tetraazanaphthalenes, and as a cautionary remark at this stage it needs to be noted that experience with related diazanaphthalenes[5] suggests that the through-bond interaction may be overestimated using Hoffmann's scheme. This is not unexpected since there is evidence that when the calculated MOs are close in energy, the CNDO/S-CI calculations may incorrectly predict their ordering.[13]

Figure 6 summarizes the energies of the n-MOs after (1) through-space only and (2) through-space plus through-bond interactions have been accounted for by our CNDO/S-CI calculations. The lowest energy $\pi^* \leftarrow n$ transition is predicted to be from an n-orbital of a_g symmetry to an antibonding π^* orbital of b_{1g} symmetry. The resulting (π^*, n) state has B_{1g} symmetry and the $\pi^* \leftarrow n$ ($S_1 \leftarrow S_0$) transition is forbidden as we observed experimentally.[8]

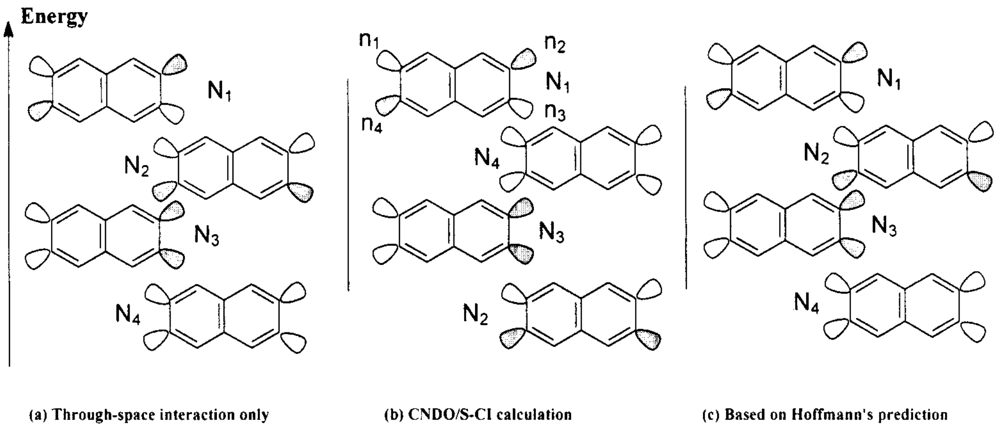
n-Orbitals of 2367-TAN. The strongest through-space interaction between the n-orbitals of 2367-TAN should involve the pairs of orbitals at each end of the molecule. The additive coupling of all four equally signed wave functions causes a stabilization of N_4 (a_g symmetry), which is therefore predicted to have the lowest energy. In the absence of through-bond coupling, the second lowest combination should be N_3 (b_{1u} symmetry). In N_3, additive coupling between the pairs of n-orbitals at each end of the molecule should cause this MO to be stabilized almost as much as N_4, since through-space interactions between lobes at opposite ends of the molecule will be minimal. However, MOs that result from combinations of n-orbitals with wave functions of opposite sign will be destabilized. N_2 and N_3 each have one nodal plane in their wave functions, but N_2 is predicted to be higher in energy owing to the destabilizing effect of the through-space interactions between the oppositely signed end lobes. Finally, N_1 (b_{3g} symmetry) is predicted to be highest in energy since it has two nodal planes in its wave function. Figure 7a illustrates the case when only through-space interactions are considered.

Our CNDO/S-CI calculations predict an orbital ordering as shown in Figure 7b. The lowest energy transition predicted by these calculations is a forbidden transition from the b_{3g} n-MO to the π^*-antibonding orbital of b_{2g} symmetry. The experimental results reported by Adembri et al.[10] show the lowest energy transition to be very weak, possibly due to a forbidden $\pi^* \leftarrow n$ transition, in agreement with our calculations.

The CNDO/S-CI calculations predict the second highest n-orbital to be N_4 (a_g symmetry) in conflict with Hoffmann's[4,14] prediction that this orbital should be the most stabilized and therefore the lowest in energy. The CNDO/S-CI calculation therefore accounts for the involvement of other σ-type orbitals in the formation of this MO, possibly including σ^*-orbitals.

Another possibility for the ordering of the n-MOs of 2367-TAN is illustrated in Figure 7c. This follows Hoffmann's prediction that the greatest interactions occur when the wave functions of the overlapping orbitals are of opposite sign. In 2367-TAN, there is greater overlap of the n-orbitals on both ends of the molecule, thus when they are opposite in sign the resulting n-MO is destabilized. The main contributing factor to the ordering of the orbitals is thus the through-space interactions. Once again, this arrangement would predict the lowest energy $\pi^* \leftarrow n$ transition to be forbidden, involving the b_{3g} n-orbital and the b_{2g} π^*-antibonding orbital. Figure 8 summarizes these results.

The unusual predictions of the ordering of n-MOs in 1458-TAN and 2367-TAN by the CNDO/S calculations prompted us to seek a way of justifying the results. To do this, we needed to observe the wave functions of the MOs after interaction of the n-orbitals with all other orbitals of the molecule. We designed a program to show contour maps of the various orbitals from the CNDO/S calculations. To rationalize the theory of through-bond coupling effects, we examined the wave functions of the highest energy σ-orbitals and estimated the extent of coupling taking place between the n- and σ-orbitals. It was expected that a comparison of the contours of the orbitals of the tetraazanaphthalenes and those of the parent molecule



(a) Through-space interaction only (b) CNDO/S-CI calculation (c) Based on Hoffmann's prediction

Figure 7. Ordering of n-molecular orbital combinations for 2367-TAN.

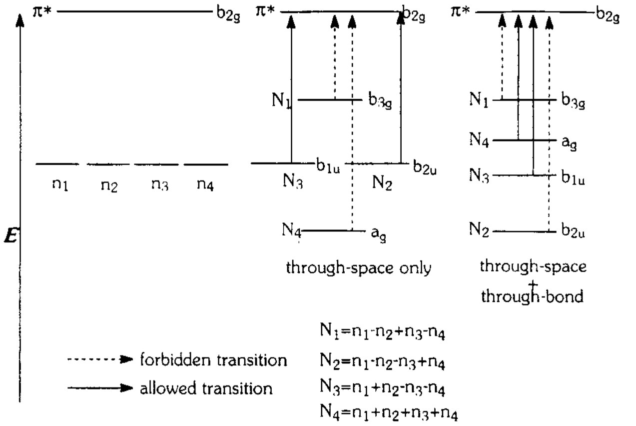


Figure 8. Energy level diagrams for 2367-TAN (not to scale) (ordering based on CNDO/S-CI calculations).

naphthalene would give an indication of the extent of this interaction. The contour maps show the sign of the wave function and the distribution of electron density. The n-orbitals and the highest energy occupied σ-orbitals of 1458-TAN and 2367-TAN and the five highest energy occupied σ-orbitals of naphthalene are illustrated in Figure 9.

Jordan et al.[2] examined the contours of the two highest energy σ-orbitals of naphthalene using semiempirical MO calculations and proposed that where the areas of greatest electron density overlap with the n-orbital electron density of the azanaphthalenes an interaction between these orbitals will cause significant energy splitting. Since our contour maps illustrate the situation after interaction and splitting has taken place, we consider that the only orbitals that would not have interacted are those that show no obvious overlap of electron density.

In the case of 1458-TAN, the n-orbital of b_{1u} symmetry appears to have no overlap with the σ-molecular orbital of b_{1u} symmetry (see Figure 9), indicating little perturbation in energy of this orbital, in conflict with our CNDO/S-CI calculations. Further attempts to develop this argument along these lines proved to be inconclusive and left us with many unanswerable questions. This qualitative attempt to get a consistent description of the coupling between the orbitals produced a number of difficulties and prompted us to look for an alternative way of explaining the relationship between energies of the n-type MOs. We propose a theoretical approach that does this in a systematic, quantitative, and instructive way.

Correlation with Naphthalene Orbitals. The electronic structure of azanaphthalenes may be viewed as arising from substitution-induced perturbations to the electronic structure of the parent molecule, naphthalene. A method for quantifying this effect is to express the MOs of the azanaphthalene in terms of those of naphthalene. In the LCAO approximation MOs, Ψ, are expressed in terms of an atomic orbital basis set ϕ. If we use the superscripts N for naphthalene and A for (say) a tetraaza derivative (see eq 1), we can write

$$\psi_i^{\mathrm{N}} = \sum_{\alpha=1}^{48} c_{\alpha i}^{\mathrm{N}}\, \phi_\alpha^{\mathrm{N}} \quad \text{and} \quad \psi_i^{\mathrm{A}} = \sum_{\alpha=1}^{44} c_{\alpha i}^{\mathrm{A}}\, \phi_\alpha^{\mathrm{A}} \qquad (1)$$

where the number of atomic orbitals shown are appropriate for the minimal valence basis set used by computational methods such as CNDO/S, and the $c_{\alpha i}$ are the MO coefficients. For simplicity, we assume there is no geometrical relaxation during nitrogen substitution, and the basis functions common to both ϕ^{A} and ϕ^{N} have the same centers and exponents and hence are equivalent. The set ϕ^{A} then differs from ϕ^{N} only in that four basis functions are missing. To correlate ϕ^{A} and ϕ^{N}, one could proceed by adding four ghost hydrogen atoms to ϕ^{A} to represent the missing hydrogen atoms (as if hydrogen atoms without their electrons and with no nuclear charge were present) and repeat the electronic structure calculation. We proceeded in a simpler fashion than adding the ghost orbitals to the basis set. We simply augmented the original MO coefficient matrix with four new MOs made up from these ghost atomic orbitals. The basis sets ϕ^{N} and ϕ^{A} thus become equivalent and are henceforth simply called ϕ and can be expressed in terms of naphthalene's MOs (see eq 2).

$$\phi_\alpha = \sum_{\alpha=1}^{48} c_{\alpha i}^{\mathrm{N}}\, \psi_\alpha^{\mathrm{N}} \qquad (2)$$

This allows the MOs of the aza derivative to be expressed as

$$\psi_i^{\mathrm{A}} = \sum_{j=1}^{44} C_{ji} \phi_j^{\mathrm{N}} \qquad (3)$$

where

$$C_{ji} = \sum_{\alpha=1}^{48} c_{\alpha j}^{\mathrm{N}}\, c_{\alpha i}^{\mathrm{A}} \qquad (4)$$

The new coefficient matrix C_{ji} thus expresses the MOs of the aza derivative in terms of those of naphthalene. In practice, factors affecting the electronic structure such as geometry changes and orbital contraction will also occur, in addition to the changes represented by this matrix. However, the matrix

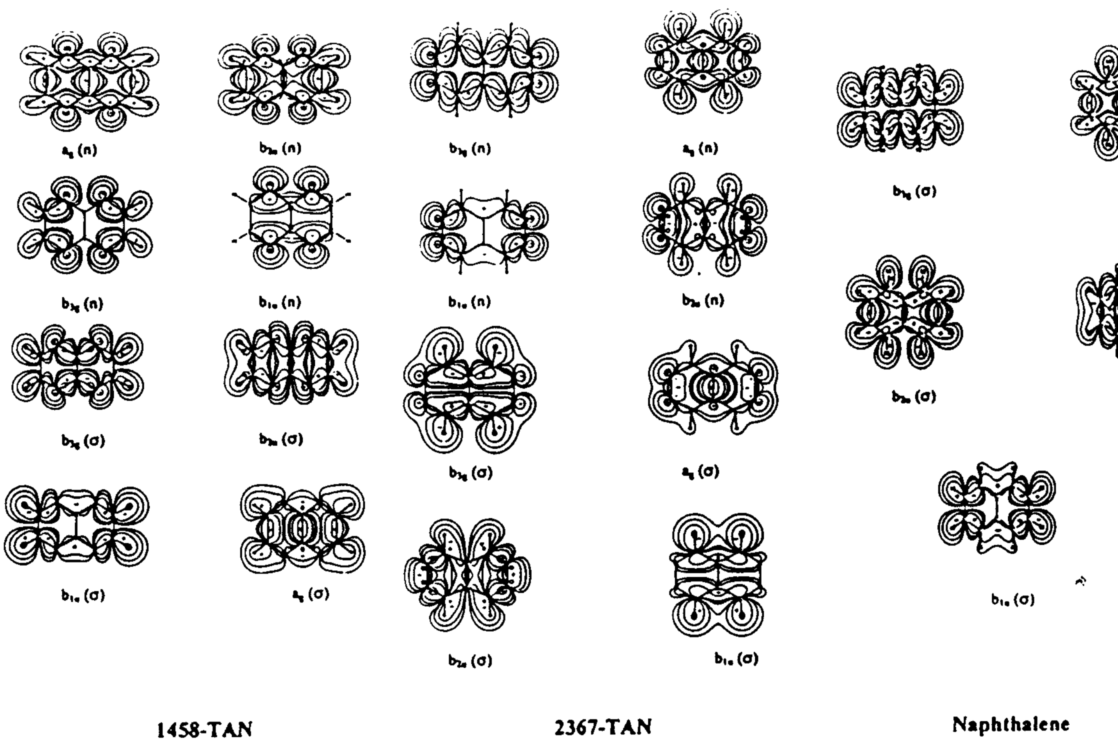


Figure 9. Contour diagrams of the highest energy molecular orbitals of 1458-TAN, 2367-TAN, and naphthalene.

gives valuable insights into how the orbitals in naphthalene shift and mix as a result of replacing a C−H group with a nitrogen atom. Qualitatively, it is expected that naphthalene C−C bonding orbitals will be pushed to much higher energies (that is, become n-orbitals) when they involve significant contamination from C−H bonds. Different orbitals will interact with different C−H bonds and hence a variation in the site of substitution will change the identity of the naphthalene orbitals that become the n-orbitals. This approach thus provides an insight into how much each of the σ-orbitals of naphthalene contributes to the formation of the n-MOs of 1458-TAN and 2367-TAN.

These calculations proved to be very enlightening. Not unexpectedly, we found that the resulting n-orbitals resemble, to varying degrees, combinations of the equivalent σ-bonding and σ*-antibonding orbitals of the parent molecule naphthalene. In effect, the σ-orbitals of naphthalene have been transformed into the n-orbitals of the TANs. This became obvious when the contour diagrams of the n-orbitals of both 1458-TAN and 2367-TAN and the σ-orbitals of naphthalene with equivalent symmetry were examined. CNDO/S-CI calculations for naphthalene give the energy ordering of the σ- and σ*-orbitals (see Figure 10). Similar calculations for 1458-TAN and 2367-TAN give energies for the n- and σ-orbitals. Only the n-orbitals for 1458-TAN and 2367-TAN are shown in Figure 10. The solid arrows in this figure indicate the naphthalene orbital that is linked most strongly to each n-orbital in 1458-TAN and 2367-TAN, and the dotted lines show secondary weaker connections between the naphthalene orbitals and the TAN n-orbitals.

It is immediately obvious that the ordering of the n-orbitals is significantly different for 1458-TAN and 2367-TAN. This marked difference was noted above, but we have been unable to justify it using Hoffmann's[4,14] arguments of through-space and through-bond coupling or by visual inspection of electron densities.[2] We believe that we can now provide a satisfactory and justifiable explanation of this ordering in terms of the extent

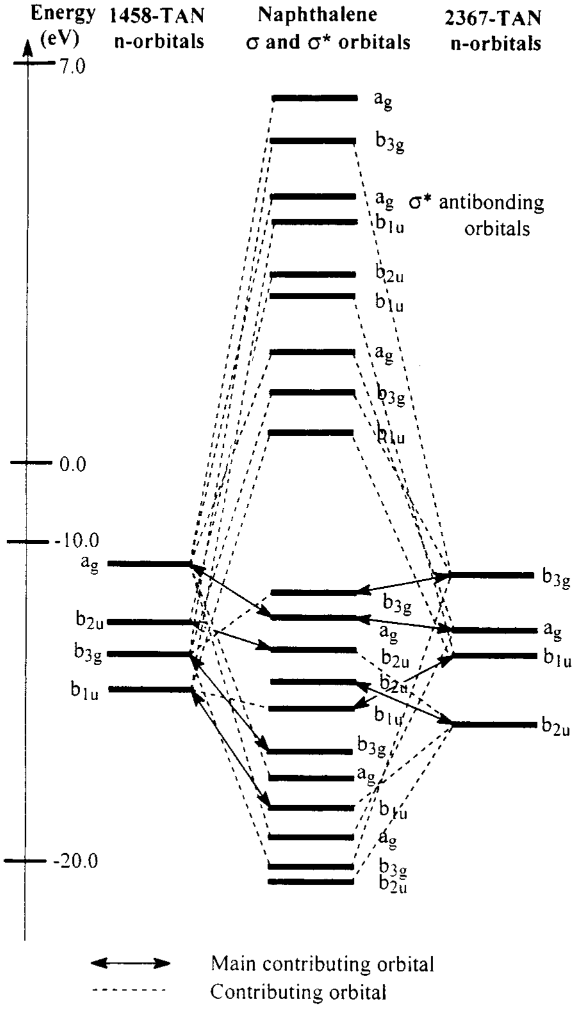


Figure 10. Energy level diagram (not to scale).

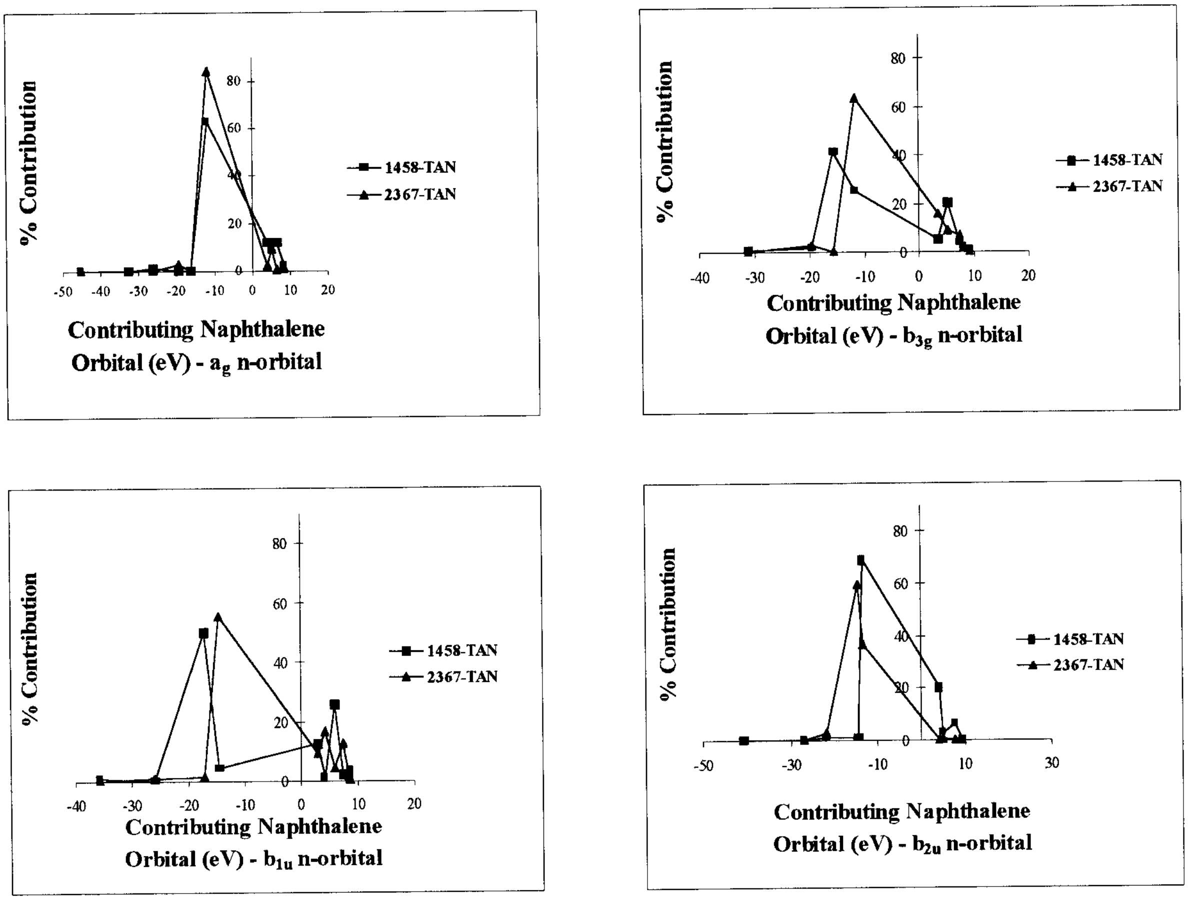


Figure 11. Percentage naphthalene σ-orbital contributions to the n-orbitals of 1458-TAN and 2367-TAN.

to which TAN σ-type orbitals have retained naphthalene-like characteristics.

Figure 10 demonstrates that the energy ordering of the n-orbitals depends on the extent to which the lower lying σ-orbitals of like symmetry and higher lying σ^*-orbitals contribute to the character of the n-orbitals. The b_{3g} n-orbital of 2367-TAN (N_1 using the notation from Figure 8) is the highest in energy, and on the basis of through-space interactions, one might expect that the same would apply in 1458-TAN. However, in 2367-TAN, the b_{3g} n-orbital is made up of a strong component of the highest energy b_{3g} σ-orbital in naphthalene and contains a significant degree of antibonding character from two higher antibonding b_{3g} σ^*-orbitals. The latter contribute to a slight destabilization of the n-orbital. In transforming the naphthalene molecule into a TAN molecule, we believe the loss of four hydrogen atoms and their stabilizing σ-bonds has introduced a degree of antibonding-like character into the system and in most instances has increased the energy of the n-orbital. In contrast, the b_{3g} n-orbital in 1458-TAN (again N_1) is lower in energy than in 2367-TAN, since it appears to be strongly linked with a lower energy σ-orbital of b_{3g} symmetry in naphthalene. This n-orbital is only weakly linked to the higher energy b_{3g} σ-orbital that plays such a strong part in determining the character of the b_{3g} n-orbital in 2367-TAN. In Figure 11, we have graphed the four symmetry species of the n-orbitals for both 1458-TAN and 2367-TAN showing the percentage contribution of each of the naphthalene orbitals in the formation of the relevant n-orbitals.

Figure 11 indicates that different b_{3g} σ-orbitals in naphthalene are transformed into the b_{3g} n-orbitals of 1458-TAN and 2367-TAN, although there are contributions from other b_{3g} orbitals as well. The main σ-orbital in naphthalene that contributes to the b_{3g} n-orbital of 2367-TAN is higher in energy than the one forming the n-orbital of 1458-TAN. The b_{3g} n-orbital in 1458-TAN is slightly higher in energy than the equivalent naphthalene σ-orbital since it has a strong contribution from an antibonding σ^*-orbital. Figure 11 shows that the same a_g σ-orbital in naphthalene is transformed into the a_g n-orbitals of both 1458-TAN and 2367-TAN. The a_g orbital of 1458-TAN is destabilized by strong contributions from three antibonding σ^*-orbitals of naphthalene, and is therefore higher in energy than the equivalent n-orbital in 2367-TAN.

Two different σ-orbitals are transformed into the b_{1u} n-orbitals of 1458-TAN and 2367-TAN (N_3), once again showing a strong contribution from antibonding orbitals as well (see Figure 11). The lower energy of the 1458-TAN b_{1u} n-orbital is a result of starting from a lower energy σ-orbital in naphthalene and being destabilized by a strong contribution from an antibonding σ^*-orbital. The b_{2u} n-orbitals of 1458-TAN and 2367-TAN (N_2) once again originate from different naphthalene σ-orbitals (see Figure 11). The b_{2u} n-orbital in 1458-TAN is raised in energy in comparison to the equivalent naphthalene orbital by a strong contribution from an antibonding orbital.

IV. Conclusions

This process of visualizing the formation of the n-orbitals from the σ-orbitals of naphthalene has not, as far as we can ascertain, been reported previously. We consider that it is a significant and useful development, which gives a more consistent explanation of the energy ordering of n-orbitals in multisubstituted nitrogen heterocycles and gives useful insights into the character of these orbitals. The previous through-space model of n-orbitals interacting with the σ-framework is, not surprisingly, an oversimplification. It has been extremely useful for rationalizing the $\pi^* \leftarrow$ n transitions of simpler heterocycles, but is almost impossible to apply consistently and quantitatively to heterocycles that contain larger numbers of nitrogens. We have found that it is more systematic and instructive to analyze the way in which the σ-orbitals of naphthalene redistribute themselves to form the azanaphthalene n-orbitals. One interesting aspect of this approach is that it has mapped the question of what causes the relative order of the n-orbitals onto the question of what causes the original ordering of the σ-orbital levels in naphthalene. The application of this model to the n-orbitals of two tetraazanaphthalenes has required a number of approximations to be made, as set out above. Further computational work will be required in order to improve these approximations, for example, by using a more extensive basis set in the calculations.

The results of this study are being used in the detailed analysis of the electronic spectra of 1458-TAN and pteridine. The next step will be to examine the spectra of some of the other azanaphthalenes, as well as some of the azabenzenes and azaphenanthrenes, to see if this approach can be adapted to rationalize the $\pi^* \leftarrow$ n transitions of a wider range of molecules.

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