THROUGH BOND INTERACTIONS OF NON-BONDING ORBITALS: THE n,π^* STATES OF AZANAPHTHALENES

A.D. JORDAN, I.G. ROSS
Chemistry Department (SGS), Australian National University, Canberra, Australia

R. HOFFMANN, J.R. SWENSON
Department of Chemistry, Cornell University, Ithaca, New York, USA

and

R. GLEITER
Physikalisch-Chemisches Institut der Universität Basel, Switzerland

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The electronic transitions of eleven azanaphthalenes as dilute solid solutions in monocrystalline hosts have been studied. Provisional assignments imply significant energy gaps between n,π^* states and lead to a low energy forbidden $\pi^*\leftarrow$n excitation in 1,5- and 1,8-diazanaphthalene. These assignments are consistent only with a significant through-bond coupling of the non-bonding orbitals, an analysis of which is presented.

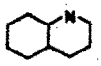
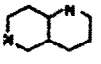
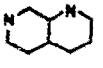
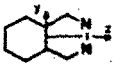
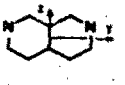
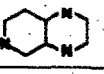
The lowest electronic transitions of nitrogen heterocycles are commonly $\pi^*\leftarrow$n transitions, involving the "non-bonding" (n) electrons of the nitrogen atoms. In molecules with two or more heteroatoms, the ordering and spacing of the n,π^* excited states provides one measure of the interactions between the n orbitals. On the assumption that these interactions are through space, it was commonly predicted [1] that, for instance, pyrazine (1,4-diazabenzene), in which the n orbitals are well separated, should show two close $\pi^*\leftarrow$n transitions, the lower one *forbidden*. In fact it is now almost certain [2] that the $\pi^*\leftarrow$n singlet–singlet absorption of pyrazine, observable over a span of 7000 cm^{-1}, consists of one allowed transition. These and many other formerly puzzling observations are rationalized by the recognition that important interactions between formally localized orbitals occur through the σ-bond framework [3–5]. The azanaphthalenes offer a further opportunity to test the alternative theories against experiment.

We have studied the low singlet←singlet transitions of eleven azanaphthalenes, as dilute solid solutions in melt-grown, monocrystalline hosts, at 4.2°K. Three polarizations (*a*, *b*, *c'*) were normally measured. The resolving power of the spectrometer was 60000. A parallel study [6] provided vapor spectra for many of the compounds. Table 1 summarizes the experimental program and the assignments of transitions. Attempts were also made to examine three tetra-azanaphthalenes, but they were insoluble in the host crystals used here (a consequence [7] of their reduced molecular volume); no suitable host has yet been found for them.

Hochstrasser and Marzzacco [8] identified two $\pi^*\leftarrow$n transitions in phthalazine (the 2,3-compound), but both were forbidden. This is contrary to simple theory. We confirmed their observations, agree with their interpretation, and have seen in our work nothing like the sudden onset of their second transition. That is, their observation remains unique, for all our other spectra show at most one $\pi^*\leftarrow$n system. Table 1 therefore gives only lower bounds to the spacings between n,π^* states, being generally the interval between the onset of absorption and the $\pi^*\leftarrow\pi$ cut off.

Some of these assignments in table 1 are necessar-

Table 1
Observed transitions and calculated levels in azanaphthalenes

Compound		Conditions of measurement[a]	Lowest observed transitions[a,b]	Separation between n,π* states obs. (eV)	Separation between n levels calc. (eV)	n level ordering calc.[c]	Lowest π* level calc.[d]
1-		NDV	DV: π; N: one n < π	–	–	–	–
2-		DXCV	π only	–	–	–	–
1,2-		NDV[e]	one n < π	>1.0	0.52	"A" "S"	–
1,3-		NDPVV[f]	one n < π	>0.5	0.69	"A" "S"	–
1,4-		NDVV[f] N[g]	one n, allowed < π	>0.45	1.37	a_1(S) b_2(A)	b_1
1,5-		NDXP	one n, forbidden < π	>0.45	1.00	a_g(S) b_u(A)	b_g
1,6-		NV	V: π; N: one n < π	>0.25	0.15	"S" "A"	–
1,7-		N	one n < π	>0.25	0.46	"A" "S"	–
1,8-		N	one n, forbidden < π	>0.3	0.70	a_1(S) b_2(A)	a_2
2,3-		N[h] ph[h]	two n, forbidden < π	0.21	0.86	b_2(A) a_1(S)	a_2, b_1
2,6-		–	–	–	1.03	a_g(S) b_u(A)	b_g
2,7-		–	–	–	0.60	b_2(A) a_1(S)	a_2, b_1
1,4,5-		NV	one n < π	>1.0	1.08[i]	–	–
1,4,6-		NV	one n < π	>0.7	0.71[i]	–	–

a) N = in naphthalene, D = in durene, X = in p-xylene, C = p-dichlorobenzene, P = as pure crystal, V = as vapor [4]. Unreferenced letters indicate this study.

b) n denotes a π*←n transition, π a π*←π transition; π*←n transitions in unsymmetrical compounds are necessarily allowed.

c) Lower energy level below, upper level above. Symmetry classification with respect to axes indicated except for C_s cases, where n combinations are classified as approximately symmetric ("S") or approximately antisymmetric ("A") with respect to interchange.

d) Only non-trivial symmetry properties listed. Where two π* levels are within 0.5 eV both are given, lower one first.

e) Ref. [9]. f) Ref. [10]. g) Ref. [11]. h) Ref. [6].

i) There are three non-bonding orbitals here. The separation listed is that between the highest energy n combination and the next one below.

ily provisional, for the spectra are not simple and are commonly perturbed in the crystal. Complicating features in crystals include

(i) vibronic activity not seen in the vapor and changes of up to 30 cm^{-1} in molecular vibration frequencies;

(ii) site splittings, double or multiple, as large as 300, perhaps 600, cm^{-1};

(iii) phonon bands, which may take different forms in spectra originating from different sites;

(iv) irregular vapor to crystal shifts, ranging from +8 to −3000 cm^{-1}, the latter being responsible, in our interpretation, for bringing into view $\pi^* \leftarrow n$ transitions in the 1- and 1,6-compounds which in the vapor lie above the $\pi^* \leftarrow \pi$ absorption;

(v) grossly perturbed polarizations, especially in naphthalene.

Conventional deep-trap theory [12] (which assumes perfect substitution in a perfect lattice) is inadequate to explain the polarization effects; e.g., one of the most irregularly polarized of the spectra is that of the 1,2-compound, in naphthalene; as the deepest trap its spectrum should be the least perturbed. Perturbations induced by durene are less drastic, but unfortunately the crystal structure of durene is such that transitions polarized along normal and long molecular axes are indistinguishable, and the naphthalene data are necessary.

The principal qualifications to table 1 are: the observable spectrum of 1,7- is short, irregular, and the analysis sketchy; the spectrum obtained for 1,8- was very weak, but wholly long-axis polarized; and in 1,5-, the most difficult of all the spectra, the origin is not missing but in naphthalene host is exclusively c' (long axis) polarized. We are obliged to attribute its appearance to molecules on sites which lack the inversion symmetry of perfect lattice sites.

We turn to a theoretical analysis of these results. With the advent of all-valence-electron molecular orbital calculations, it has become clear that formally equivalent lone pairs interact strongly with each other through bonds, as well as through space [3–5]. For the diazabenzenes 1–3, the clearcut prediction was made that the nitrogen non-bonding orbital combinations $n_1 + n_2$ and $n_1 - n_2$ should be significantly split in one-electron energy. The ordering of these levels is indicated below each structure, along with the computed energy splittings (fig. 1).

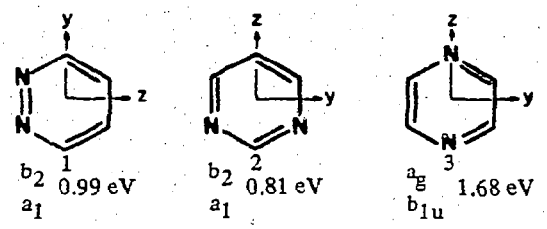


Fig. 1.

Photoelectron spectroscopy confirms the magnitude of the splitting (experimentally 2.00 eV for 1, 1.50 eV for 2, 1.72 eV for 3) but as yet has not provided us with an assignment of the ionizing levels [13]. When the lowest lying π^* level is examined the conclusion is reached that in 1, 2 and 3 the lower energy $\pi^* \leftarrow n$ transition is the allowed one. A recent ab initio study of the electronic excited states of pyrazine is in accord with our arguments [14]. The strength of any spectroscopic test of our theoretical conclusions would be augmented if we could predict a case in which the lower energy $\pi^* \leftarrow n$ transition is the *forbidden* one. The diazanaphthalenes present such an opportunity.

Table 1 shows, in addition to the experimental conclusions, the computed lone pair splitting patterns, as well as the symmetry of the lowest unoccupied π^* levels. The method of calculation is the extended Hückel theory [15] †. The actual calculated level energies are not considered reliable, and accordingly only the lone pair splitting is explicitly reported. Obviously term values are not identical to simple differences between one-electron energy levels. Nevertheless our experience, as well as the magnitude of the calculated splittings, leads us to suggest that the computed level ordering will be reflected by the experimental state order. Examination of the orbital symmetries in table 1 reveals a prediction of forbidden lower energy $\pi^* \leftarrow n$ transitions in 1,5-, 1,8- and 2,6-diazanaphthalenes, in agreement with the experimental results for the two cases studied ‡.

An interpretation of the computed lone pair splitting patterns follows. Firstly, we explore the correlation with our general analysis of the conformational dependence

† The diazanaphthalene ring is idealized with all CC and CN distances 1.40 A, all CH 1.08 A. The hydrogen exponent is 1.3.

‡ Further information on the level ordering should be forthcoming from photoelectron spectroscopy. A study [16] of some diazanaphthalenes has been published.

of through space and through bond coupling [3,4]; secondly, we relate these arguments to the specific σ structure of the naphthalene framework. We shall refer to the diazanaphthalenes by their nitrogen positions; lone pairs combinations will be called S when they are symmetric or approximately so under the real or pseudo operation interchanging them, A when they are antisymmetric.

1,2 and 2,3, just like pyridazine, generate the S below A pattern characteristic of dominant through space coupling. 1,3 with S below A, 1,8 with A below S, are consistent with our general analysis, and emphasize the sharp conformational dependence of the coupling pattern. The clearest manifestation of the through bond effect may be in 1,4 and 1,5 where A is below S, as expected [3–5]. The remaining cases have a multiplicity of coupling σ-bond paths. They are less straightforward to analyze, and in particular the sizable 2,6 splitting was not anticipated.

The specific analysis begins with the CC σ orbitals of naphthalene†. An extended Hückel calculation shows that the highest occupied σ level is b_{1g}, the next one below it a_g ‡. These orbitals, whose approximate shape is maintained in the diazanaphthalenes, are shown schematically in fig. 2.

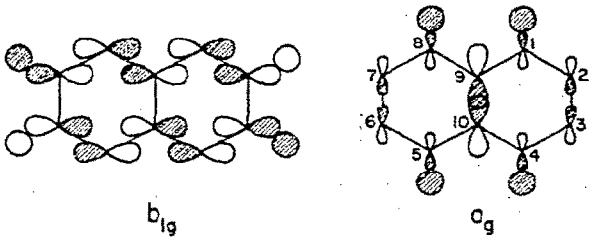


Fig. 2.

We now reconsider some of the interesting cases. For 1,4-diazanaphthalene b_{1g} is antisymmetric (b_2 in C_{2v}) with respect to lone pair interchange, a_g symmetric (a_1 in C_{2v}). In a perturbation theory analysis of the interaction of two N lone pairs, a_1 and b_2 in C_{2v}, with these σ orbitals one would expect the energy denominator to favour interaction (destabilization) with the b_{1g} naphthalene framework orbital. Note, however, that the overlap of a 1 or 4 N lone pair with b_{1g} is minimal, whereas the vicinal overlap [3] with a_g, which is primarily the 9–10 σ bond, is sizable. Thus the a_1 N lone pair combination and the a_1 (a_g) framework orbital interact more, leading to the lone pair ordering of b_2 below a_1.

Next consider 1,8-diazanaphthalene. Here again the b_{1g} (b_2 in C_{2v}) skeletal orbital can in principle interact with the b_2 lone pair combination, but in fact the overlap is small. a_1 interacts more with a_g, leading once again to the ordering b_2 below a_1. For 1,5- and 2,6-diazanaphthalene both the high-lying framework orbitals b_{1g} and a_g are symmetric with respect to lone pair interchange. They thus clearly destabilize the a_g lone pair combination, while b_u is less perturbed. For an analysis of the 2,7-diazanaphthalene we focus on the symmetry properties of b_{1g}. It is now antisymmetric with respect to 2,7 orbital interchange. Accordingly the b_2 lone pair combination is destabilized. From this simple theoretical analysis we can thus interpret the entire spectrum of non-bonding orbital interactions in azanaphthalenes.

An interesting further prediction which we can make is of the presence in 1,4,5,8-tetrazanaphthalene of a highly destabilized non-bonding orbital combination of a_g symmetry. Coupled with a very low-lying b_{3g} π^* orbital this should result in a low energy forbidden $\pi^* \leftarrow n$ transition in this heterocycle.

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† Strictly speaking we should include the effect of the σ^* orbitals as well. For interaction with low-lying N lone pairs these are not nearly as important as the σ levels, which are much closer in energy.

‡ Ab initio calculations also identify the two highest σ orbitals as being of this symmetry, but reverse their ordering. See ref. [17].

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