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Comparison of the Electronic Transitions of Unconjugated Thiones and Imines

An exercise in the application of symmetry selection rules

It is the purpose of this paper to show how symmetry selection rules can be used to determine whether certain of the electronic transitions exhibited by the title compounds are allowed or forbidden by symmetry. Our treatment assumes an elementary knowledge of symmetry operations, point groups, symmetry species, and character tables as given in other sources (1-6).

Recent investigations on the imine chromophores have established the existence and type of certain electronic transitions (7-10). Using the symmetry selection rules, we should be able to obtain agreement with the experimental data shown in Table 1. In Figure 1 is illustrated the orientation of the imine chromophore about the Cartesian coordinate system. The molecular orbital picture in Figure 2 assumes sp^2 hybridization based on experimental data which shows the $C=N-R$ bond angle to be approximately 119° (11, 12). The basic rules of symmetry allow us to assign this chromophore to the C_s point group. If we now operate on each orbital of the chromophore separately with I and σ_{xz} (the symmetry operations of the C_s point group) we obtain the species representation for the orbitals as shown in the C_s character table (Table 2). Only two different species are obtained, and they are designated A' and A'' .

At this point we must introduce a quantity known as the dipole moment vector, \vec{M} . This quantity is related to the average charge displacement during an electronic transition. Like any vector, it can be resolved into three components, one along each of three mutually perpendicular axes. These component vectors are now associated with the Cartesian coordinate system of the point group C_s , and each of the components M_x , M_y , and M_z are operated on by the symmetry operations of the group. An operation either leaves the direction of the component vector unchanged, resulting in a +1 character, or reverses the direction of the vector, (-1 character). Each component vector can then be assigned to the proper symmetry species, and these are indicated in the C_s character table.

The symmetry selection rule with which our discussion is concerned states that for a transition to be allowed, the product of the symmetries of the ground and excited states must be of the same species as at least one component of the dipole moment vector. If this is not the case, the transition is said to be forbidden by symmetry.

Returning now to a description of the electronic transition of the imine chromophores, let us look at the lowest energy $n \rightarrow \pi^*$ transition. The ground state can be represented as $\sigma_a'^2$, $n_a'^2$, $\pi_a'^2$ and this becomes equivalent to an A' species. The $n \rightarrow \pi^*$ state can be represented as $\sigma_a'^2$, n_a' , $\pi_a''^2$, $\pi_a''^*$ which becomes an A'' species. The $n \rightarrow \pi^*$ transition can then be represented as $A'' \leftarrow A'$. The product of $\psi_g \psi_f = A''$ and since M_z transforms as this species, the transition is said to be symmetry allowed.

Experimental data show an $n \rightarrow \pi^*$ transition for the imine chromophore occurring at 245 nm with a ϵ of 200 (8). This is

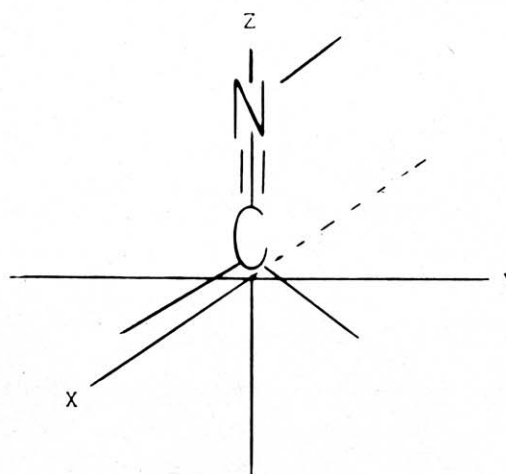


Figure 1. Orientation of the imine chromophore in a Cartesian coordinate system.

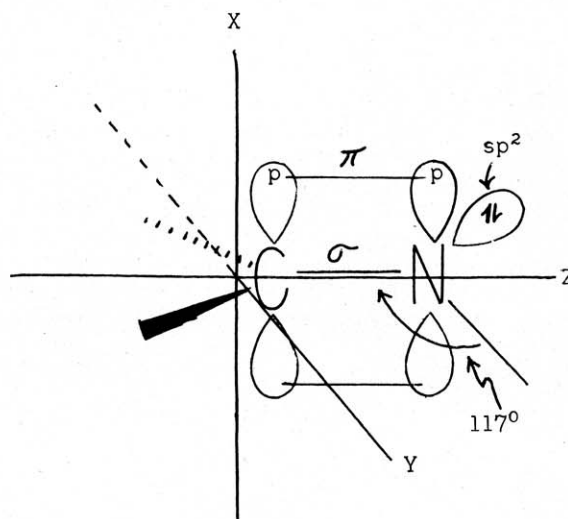


Figure 2. Partial molecular orbital representation of the imine chromophore.

Table 1. Absorption Maxima and Molar Absorptivities for Compounds Containing the Simple Unconjugated Azomethine Chromophore

Compound	$n \rightarrow \pi^*$ Transition				$\pi \rightarrow \pi^*$ Transition			
	Cyclohexane λ_{max}^a	Ethanol ϵ_{max}^b	Ethanol λ_{max}^a	Ethanol ϵ_{max}^b	-Heptane λ_{max}^a	-Heptane ϵ_{max}^b	TMP ^c λ_{max}^a	TMP ^c ϵ_{max}^b
N-isopropylidene-butylamine	246	140	232	200	179	8900	183	...
N-cyclohexylidene-butylamine	245 _s	...	238	230	180	9600	185	...

^a In nanometers.

^b Liters/mole cm.

^c Trimethyl phosphate.

^d Reference (10).

Paper 1 in the series appeared in J. CHEM. EDUC., 47, 709 (1970).

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Table 2. Character Table for the C_s Point Group

C_s	I	σ_{xy}	
A'	+1	+1	M_x, M_y
A''	+1	-1	M_z

Table 3. Character Table For the C_{2v} Point Group

C_{2v}	I	$C_{2(z)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	
A_1	+	+	+	+	M_z
A_2	+	+	-	-	
B_1	+	-	+	-	M_x
B_2	+	-	-	+	M_y

greater than the corresponding ϵ for the same transition in the thiocarbonyl chromophore which is forbidden by symmetry. All other electronic transitions of the imine chromophore are also allowed by symmetry since there is at least one dipole moment vector assigned to each species in the character table.

The thiocarbonyl chromophore, like that of the carbonyl, belongs to C_{2v} point group. One pair of non-bonding electrons is best represented in a $3p$ orbital, the other in a non-bonding $3s$ orbital or in other words there is no hybridization about the sulfur atom in the thiocarbonyl chromophore. Using an approach similar to that for the imine chromophore and now using the C_{2v} character table (Table 3), we arrive at the following classification of the electronic transitions of the thiocarbonyl chromophore which fit the observed data; 500 nm ($\epsilon = 5$) $n \rightarrow \pi^*$ ($A_2 \leftarrow A_1$) symmetry forbidden; 500 nm ($\epsilon = 5000$) $\pi \rightarrow \pi^*$ ($A_1 \leftarrow A_1$) symmetry allowed (13).

In conclusion it is possible to understand why certain electronic transitions are allowed or forbidden using symmetry considerations. It should be emphasized that a simplified

picture was given so that the actual use of symmetry in understanding electronic transitions could be demonstrated. This representation, however, is an oversimplification, primarily because we have considered the geometry of the ground and excited states to be the same. This is usually not true, because the orbitals in excited states reorient themselves in order to minimize such forces as dipole-dipole interactions. Such considerations are as yet not fully understood, and much work in this area is continuing to further elucidate the theory of electronic transitions. Another neglected area in this discussion is the spin allowed or spin forbidden states. It is obvious that all the possible transitions can either proceed to singlet or triplet state. Of these, the triplet is spin forbidden and would make a transition already forbidden by symmetry even less likely to occur.

We feel the above discussion presents information which is absolutely necessary for anyone attempting to understand ultraviolet absorption spectroscopy as related to organic structural analysis.

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