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MOLECULAR ORBITAL STUDIES ON THE OPTICAL ACTIVITY OF CHIRAL NITROSAMINES AND NITRAMINES

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Abstract—The chiroptical properties of the two lowest energy singlet–singlet transitions in a series of N-nitrosopiperidine derivatives are examined on a CNDO/S-CI molecular orbital (MO) model in which rotatory strengths are calculated directly from total molecular electronic wave functions. Similar calculations are carried out for the three lowest energy singlet–singlet transitions in a series of chiral N-nitropiperidine derivatives. The results obtained for the low energy $n \rightarrow \pi^*$ transitions in these compounds are compared to those predicted by sector rules proposed for chiral N-nitrosamine and N-nitramine systems.

INTRODUCTION

The Cotton effect (CE) associated with the weak UV band centered near 370 nm for chiral N-nitrosamine systems has frequently been used in making stereochemical correlations among compounds possessing the N-nitrosamino chromophoric group. Snatzke *et al.*[1] first proposed a sector rule for this near UV CE which permitted assignments of absolute configuration to be made directly from the observed sign of the CE. This sector rule was based on what they presumed to be the nodal properties of the orbitals involved in the 370 nm transition (assigned as $n_N \rightarrow \pi^*$). The sign pattern of the sector rule was based on the experimentally determined sign of the 370 nm CE for N-nitrosopipecoline which was used as a model compound and assumed to be of equatorial conformation. Both the validity and generality of this sector rule have been questioned in the recent literature[2–4] and very recently Polonski and Prajer[5] have proposed a new, modified sector rule for the 370 nm CE of chiral N-nitrosamine compounds. Polonski and Prajer[6] have also proposed a sector rule for the 270 nm CE observed for chiral N-nitramines.

In the present study we investigate the chiroptical properties associated with the two lowest energy singlet–singlet electronic transitions in a series of chiral N-nitrosopiperidine derivatives using the CNDO/S-CI MO model. Our procedure is to calculate the ground state electronic wave functions of the molecular systems in the CNDO/S-MO approximation[7] and then construct electronic excited states in the virtual orbital-configuration interaction (CI) approximation. These wave functions are then used to calculate, directly, the oscillator strengths, rotatory strengths, and dissymmetry factors associated with the two lowest energy singlet–singlet transitions. Direct calculations of molecular chiroptical properties from MO models have proved useful in a number of cases for establishing spectra-structure relationships and for testing the validity of semiempirically derived sector rules.[8] Detailed and rigorous tests of sector rules require characterizations of the electronic structural features of chromophoric groups which are beyond the capability of MO models such as CNDO/S. However, calculations based on CNDO/S-CI wave functions do provide alternative representations of molecular optical activity which may be usefully compared to those provided by sector rule pictures.

Nineteen chiral N-nitrosopiperidine structures are examined in the present study along with three chiral N-nitropiperidine structures.

METHODS OF CALCULATION

Ground state electronic wave functions were calculated in the CNDO/S-MO approximation. Excited electronic state wave functions were constructed in the virtual orbital-configuration interaction (CI) approximation with only the five lowest energy singly-excited configurations included in the calculations on the N-nitrosopiperidine structures reported here. The ten lowest energy singly-excited configurations were included in our CI calculations on the N-nitropiperidine derivatives. Rotatory strengths, oscillator strengths, and dissymmetry factors were calculated directly from these wave functions for the two lowest energy singlet–singlet transitions in each N-nitrosamino structure and for the three lowest energy singlet–singlet transitions in each N-nitramine structure. Electric dipole transition integrals were calculated in the dipole velocity formalism, and all one-, two- and three-center terms were included in calculating both the electric dipole and the magnetic dipole transition moments.

Rotatory strengths are expressed in terms of "reduced rotatory strengths" where, for the electronic transition $i \rightarrow j$,

$$[R_{ij}] = \text{reduced rotatory strength}$$

$$= (100/\beta\mathscr{D})\,\mathrm{Im}\langle\psi_i|\hat{\mu}|\psi_j\rangle\cdot\langle\psi_j|\hat{m}|\psi_i\rangle. \tag{1}$$

In eqn (1), β is the Bohr magneton, $\mathscr{D}$ is the Debye unit, $\hat{\mu}$ is the electric dipole operator, and $\hat{m}$ is the magnetic dipole operator. Dissymmetry factors are defined by,

$$g_{ij} = 4R_{ij}/D_{ij} \tag{2}$$

where,

$$R_{ij} = \mathrm{Im}\langle\psi_i|\hat{\mu}|\psi_j\rangle\cdot\langle\psi_j|\hat{m}|\psi_i\rangle \tag{3}$$

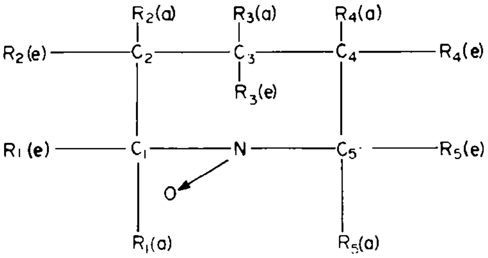
and,

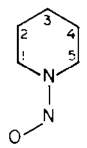
$$D_{ij} = |\langle\psi_i|\hat{\mu}|\psi_j\rangle|^2. \tag{4}$$

STRUCTURES

(A) N-*Nitrosopiperidines*

We depict the N-nitrosopiperidine derivative as follows:



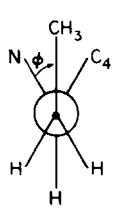


where the N–O bond lies in the plane defined by the C_1, C_5 and N(piperidine) atoms and points away from the C_5 atom. The unsubstituted structure (**1**) is optically active since it is lacking in any improper symmetry axis and may exist in two enantiomeric forms.

Seven monomethyl-substituted derivatives were examined. These are listed as follows: (**2**), $R_5(e) = Me$; (**3**), $R_5(a) = Me$; (**4**), $R_1(a) = Me$; (**5**), $R_4(e) = Me$; (**6**), $R_2(e) = Me$; (**7**), $R_3(a) = Me$; (**8**), $R_3(e) = Me$.

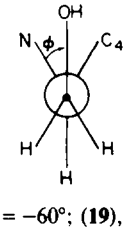
Four dimethyl-substituted derivatives were studied. These are listed as follows: (**9**), $R_5(e) = R_1(a) = Me$; (**10**), $R_5(a) = R_4(e) = Me$; (**11**), $R_5(e) = R_2(e) = Me$; (**12**), $R_5(a) = R_2(e) = Me$.

Four monoethyl-substituted derivatives were examined. In each of these structures, $R_5(e) = Et$. These four structures differ with respect to rotation about the C_5-Et bond, and are defined by the angle ϕ in the Newman projection shown below:



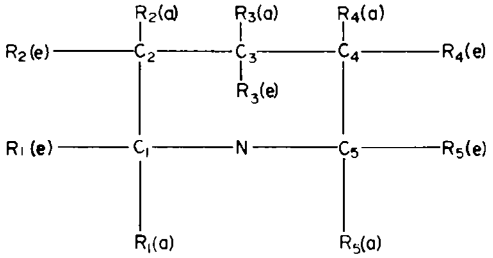
(**13**), $\phi = 60°$; (**14**), $\phi = -60°$; (**15**), $\phi = 180°$; (**16**), $\phi = -120°$.

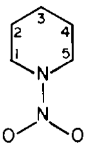
Three monomethanol-substituted structures were examined. In each of these structures, $R_5(e) = CH_2OH$. These structures differ with respect to rotation about the C_5–CH_2OH bond, and are defined by the angle ϕ in the Newman projection shown below:



(**17**), $\phi = 60°$; (**18**), $\phi = -60°$; (**19**), $\phi = 180°$.

(B) N-*Nitropiperidines*





The unsubstituted N-nitropiperidine structure is, of course, nonchiral (possessing C_s symmetry). The three chiral N-nitropiperidine derivatives examined in the present study are listed as: (**20**), $R_4(e) = Me$; (**21**), $R_1(a) = Me$; (**22**), $R_5(a) = R_4(e) = Me$.

(c) *Ring structures*

In each of the structures examined in this study the six-membered piperidine ring was assumed to exist in a chair conformation.

RESULTS

(A) N-*Nitrosopiperidine*

The lowest unoccupied molecular orbital (LUMO) calculated for each of the N-nitrosopiperidine structures (**1–19**) may be characterized as an antibonding pi (π^*) orbital delocalized over the N-nitrosamino chromophoric moiety (NNO) with maximum amplitude on the nitroso N atom. The highest occupied molecular orbital (HOMO) is calculated to be of the π^0 type with a node (zero amplitude) at the nitroso N atom and large amplitude at the O atom and at the amino N (ring) atom. The next highest occupied molecular orbital (NHOMO) is calculated to have significant in-plane (of the N-nitrosamino group) pi bonding interactions between the N and O atoms of the NO group, but has maximum amplitude on the O atom. We shall designate this NHOMO as n although it must be understood that it cannot be described as either a "nonbonding" oxygen orbital or a "nonbonding" nitrogen orbital.

The lowest energy singlet excited state calculated for each structure is comprised almost entirely of the $n\pi^*$ configuration (the CI coefficient for this configuration is 0.980). The second lowest energy singlet excited state calculated for each structure is comprised almost entirely of the $\pi^0\pi^*$ configuration (0.999 CI coefficient). The first two singlet–singlet transitions may be characterized then as $n \rightarrow \pi^*$ and $\pi^0 \rightarrow \pi^*$ excitations, respectively, localized on the N-nitrosamino chromophoric moiety. Each of these transitions involve significant charge-transfer ***within*** the NNO group. The electron density differences calculated for the N(nitroso), O and N(amino) atoms for the $n \rightarrow \pi^*$ and $\pi^0 \rightarrow \pi^*$ transitions in structure **1** are listed in Table 1.

The optical properties calculated for the $n \rightarrow \pi^*$ and $\pi^0 \rightarrow \pi^*$ transitions in structures **1–19** are displayed in Table 2.

Table 1. Electron density differences between ground and excited states in the $n \to \pi^*$ and $\pi^0 \to \pi^*$ transitions of structure 1

ATOM	$n \to \pi^*$	$\pi^0 \to \pi^*$
O	-0.298	0.091
N(nitroso)	0.334	0.591
N(amino)	0.029	-0.508

(B) N-*Nitropiperidines*

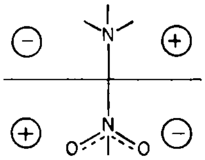
The LUMO calculated for each of the N-nitropiperidine structures (**20–22**) may be characterized as an antibonding pi (π^*) orbital delocalized over the nitro (NO_2) group with maximum amplitude on the N atom. The HOMO is calculated to be of the π^0 type with a node at the nitro group N atom, maximum amplitude on the amino N atom, and some amplitude on each of the O atoms. The next *two* occupied MO's may be described essentially as "nonbonding" orbitals localized on the O atoms. These latter orbitals have maximum amplitude in the plane of the NNO_2 group.

The two lowest energy singlet–singlet transitions may be assigned as $n_0 \to \pi^*$. These transitions involve significant charge-transfer to the N atom of the NO_2 group (about 0.55 electron units in each case). The third singlet–singlet transition may be described as a nearly pure $\pi^0 \to \pi^*$ excitation with a large transfer of charge density from the amino N (ring) atom to the nitro group N atom.

The optical properties calculated for the three lowest energy singlet–singlet transitions in structures **20–22** are listed in Table 3.

DISCUSSION

The sector rule proposed by Polonski and Prajer[6] for the lowest energy $n \to \pi^*$ transition in N-nitramine compounds is depicted as follows:



signs are for upper sectors

According to this sector rule, both structures **20** and **21** should exhibit positive $n \to \pi^*$ Cotton effects, in

Table 2. Optical properties calculated for the $n \to \pi^*$ and $\pi^0 \to \pi^*$ transitions in structures 1–19

Structure	ΔE(ev)	ε^(a)^	[R]	|g|	Transition
1	2.64	0.0029	- 0.87	0.0001	$n \to \pi^*$
	6.00	0.3751	- 1.24	0.0001	$\pi^0 \to \pi^*$
2	2.65	0.0029	2.19	0.0002	$n \to \pi^*$
	6.02	0.3791	0.05	-	$\pi^0 \to \pi^*$
3	2.66	0.0031	2.99	0.0003	$n \to \pi^*$
	5.98	0.3740	- 1.37	0.0002	$\pi^0 \to \pi^*$
4	2.66	0.0021	- 2.67	0.0003	$n \to \pi^*$
	5.97	0.3712	1.09	0.9991	$\pi^0 \to \pi^*$
5	2.67	0.0029	0.52	0.0001	$n \to \pi^*$
	6.01	0.3738	- 1.01	0.0001	$\pi^0 \to \pi^*$
6	2.65	0.0029	0.94	0.0001	$n \to \pi^*$
	5.98	0.3773	- 0.11	-	$\pi^0 \to \pi^*$
7	2.64	0.0030	- 2.26	0.0002	$n \to \pi^*$
	6.02	0.3713	- 1.56	0.0002	$\pi^0 \to \pi^*$
8	2.64	0.0030	- 2.49	0.0003	$n \to \pi^*$
	6.02	0.3720	- 0.86	0.0001	$\pi^0 \to \pi^*$
9	2.66	0.0028	7.27	0.0004	$n \to \pi^*$
	5.98	0.3751	- 0.63	0.0004	$\pi^0 \to \pi^*$
10	2.70	0.0028	40.80	0.0032	$n \to \pi^*$
	5.98	0.3737	3.35	0.0019	$\pi^0 \to \pi^*$
11	2.65	0.0029	24.91	0.0022	$n \to \pi^*$
	5.99	0.3820	- 2.86	0.0015	$\pi^0 \to \pi^*$
12	2.67	0.0028	37.07	0.0020	$n \to \pi^*$
	5.97	0.3723	1.76	0.0009	$\pi^0 \to \pi^*$
13	2.66	0.0051	33.26	0.0022	$n \to \pi^*$
	5.98	0.3585	- 1.43	0.0010	$\pi^0 \to \pi^*$
14	2.68	0.0050	17.85	0.0010	$n \to \pi^*$
	5.97	0.3566	0.83	0.0004	$\pi^0 \to \pi^*$
15	2.68	0.0029	- 5.20	0.0003	$n \to \pi^*$
	5.98	0.3837	0.32	0.0002	$\pi^0 \to \pi^*$
16	2.70	0.0030	-45.85	0.0015	$n \to \pi^*$
	5.96	0.3798	4.76	0.0020	$\pi^0 \to \pi^*$
17	2.64	0.0029	13.51	0.0010	$n \to \pi^*$
	6.00	0.3788	6.40	0.0022	$\pi^0 \to \pi^*$

Table 2 (*Cont*)

Structure	ΔE(ev)	f [(a)]	[R]	|q|	Transition
18	2.66	0.0030	15.40	0.0023	$n\to\pi^*$
	6.05	0.3751	- 7.77	0.0025	$\pi^0\to\pi^*$
19	2.65	0.0031	43.04	0.0061	$n\to\pi^*$
	6.05	0.3757	- 4.24	0.0015	$\pi^0\to\pi^*$

(a) oscillator strength

Table 3. Optical properties calculated for the three lowest energy transitions in structures **20–22**

Structure	ΔE(ev)	f [(a)]	[R]	|q|	Transition
20	4.49	-	41.17	0.0310	$n_1\to\pi^*$
	4.65	0.0001	0.69	0.0021	$n_2\to\pi^*$
	6.02	0.1921	- 6.37	0.0171	$\pi^0\to\pi^*$
21	4.45	-	31.82	0.0193	$n_1\to\pi^*$
	4.68	-	19.87	0.0128	$n_2\to\pi^*$
	5.95	0.1941	11.95	0.0013	$\pi^0\to\pi^*$
22	4.53	0.0001	-14.84	0.0103	$n_1\to\pi^*$
	4.69	0.0002	-18.42	0.0067	$n_2\to\pi^*$
	6.04	0.2096	- 9.62	0.0229	$\pi^0\to\pi^*$

(a) oscillator strength

agreement with the calculated results shown in Table 3. In structure **22** one of the substituents, R_5(a), lies in a negative sector while the other substituent, R_4(e), lies in a positive sector. The R_5(a) substituent, however, lies closest to the NNO_2 chromophoric moiety and, as expected, dominates the sign of the $n\to\pi^*$ Cotton effect. That is, the rotatory strengths calculated for the two nearly degenerate $n\to\pi^*$ transitions are negative in sign. Polonski and Prajer[6] reported only very weak absorption in the 270 nm region where the first Cotton effect is observed for **20**. This is in agreement with the very small oscillator strengths calculated for the $n\to\pi^*$ transitions.

It is readily apparent from the data presented in Table 2 that a clear-cut, simple sector rule does not emerge for the N-nitrosopiperidine derivatives examined in this study. Neither Snatzke's original sector rule[1] nor Polonski and Prajer's more recently proposed sector rule[5] is adequate for correlating the signs of the computed $n\to\pi^*$ rotatory strengths with specific structure types. The calculated data reflect the extreme sensitivity of $n\to\pi^*$ rotatory strength to: (1) the position of ring substitution; (2) the number and relative disposition of ring substituents; and, (3) rotameric isomerism of individual substituent groups (see the results for structures **13–19**). The calculated $n\to\pi^*$ rotatory strength data for the N-nitrosopiperidine structures would appear to be in consonance with the findings of Ripperger and Schreiber[4] who, after studying the CD of about thirty chiral nitrosamines, concluded that application of Snatzke's sector rule provided only ambiguous information regarding absolute configuration. The relatively small oscillator strengths calculated for the $n\to\pi^*$ transitions in the N-nitrosamine structures (**1–19**) are in good agreement with the low extinction coefficients observed for the 370 nm absorption band in related compounds ($\epsilon < 120$). However, the $n\to\pi^*$ transition energies calculated with our CNDO/S-CI model are too low by about 20%.

The results obtained in this study clearly demonstrate the inadequacy of the simplistic sector rules offered by Snatzke[1] and by Polonski and Prajer[5] for the $n\to\pi^*$ transition of chiral N-nitrosopiperidine compounds. The low symmetry (C_s) of the N-nitrosoamino chromophore (NNO) and the nature of our calculational model preclude a detailed, diagnostic analysis of the results presented here. However, a number of general observations and comments may be made. First, the "n" orbital of the $n\to\pi^*$ transition was found to be localized primarily on the O atom of the N-nitrosoamino chromophore rather than on the adjacent N atom (as was presumed in the formulation of the original sector rules[1,5]). Second, the magnetic dipole transition moment associated with the $n\to\pi^*$ transition was calculated to be substantial (0.7–0.9 Bohr magneton) for each of the structures examined, and its orientation was found to be nearly collinear (±10°) with the NO bond of the N-nitrosoamino group. Third, although the dipole strength of the $n\to\pi^*$ transition remained essentially unchanged by substitution about the piperidine ring, the orientation of the electric dipole transition vector was found to be extremely sensitive to substitution. This orientation dependence of the $n\to\pi^*$ electric dipole transition vector upon ring substitution accounts in large part for modulation of $n\to\pi^*$ rotatory strength as a function of ring substitution. (Recall that it is the projection of the electric dipole transition vector upon the magnetic dipole transition vector which determines the sign and magnitude of the rotatory strength quantity—see Eqn (1).)

Considering the monomethyl derivatives of N-nitrosopiperidine (structures **2–8**), we note that the $n\to\pi^*$ rotatory strength is largest for structures **2**, **3**, **4**, **7** and **8**, and is calculated to be smallest for structures **5** and **6**. The larger $n\to\pi^*$ rotatory strengths for **2**, **3**, **4** and **7** vs **5** and **6** may be explained in terms of the relative distances between the Me substituents and the chromophoric center in these structures if one assumes (as in the traditional view based on the "one-electron" theory of molecular optical activity) that "vicinal" or "through-space" substituent-chromophore interactions are of dominant importance in communicating remote structural chirality to the inherently symmetric chromophore. The moderately large $n \rightarrow \pi^*$ rotatory strength calculated for structure **8**, however, cannot be accounted for on this basis.

The results obtained for the $n \rightarrow \pi^*$ rotatory strengths of the dimethyl-substituted N-nitrosopiperidine structures, **9–12**, cannot be explained at all in terms of simple additivity or through-space (vicinal) interaction concepts. If substituent groups contributed additively to the $n \rightarrow \pi^*$ rotatory strengths of these compounds, then the following results should obtain:

$$R_{n\pi^*}(\mathbf{9}) = R_{n\pi^*}(\mathbf{2}) + R_{n\pi^*}(\mathbf{4})$$
$$R_{n\pi^*}(\mathbf{10}) = R_{n\pi^*}(\mathbf{3}) + R_{n\pi^*}(\mathbf{5})$$
$$R_{n\pi^*}(\mathbf{11}) = R_{n\pi^*}(\mathbf{2}) + R_{n\pi^*}(\mathbf{6})$$
$$R_{n\pi^*}(\mathbf{12}) = R_{n\pi^*}(\mathbf{3}) + R_{n\pi^*}(\mathbf{6})$$

As is obvious from the data presented in Table 2, these relationships do not hold (even approximately). Adding substituents at remote sites to structures which already have a substituent at a close-in site (C_1 or C_5) results in an enormous enhancement of $n \rightarrow \pi^*$ rotatory strength (compare the results for **3** vs those for **10** and **12**). These results suggest that substituents cannot be treated one-at-a-time and that simple substituent-chromophore pairwise interactions do not provide an adequate representation of the chiral N-nitrosopiperidine derivatives. Simple first-order perturbation models based on the "one-electron" theory of optical activity are restricted to such perturber-chromophore pairwise interactions and lead to predictions of additivity with respect to perturber contributions to the rotatory strengths of chromophoric transitions. Direct calculational models based on MO calculations (such as those employed in the present study) have incorporated in them interactions between all parts of the molecular system.

Our results are not amenable to an analysis which would reveal whether the enhanced $n \rightarrow \pi^*$ rotatory strengths of the dimethyl derivatives (**9–12**) are due to 3-way substituent-substituent-chromophore through-space interactions or to subtle through-bond interactions. Kirk and Klyne[9] have asserted that the $n \rightarrow \pi^*$ rotatory strengths of carbonyl compounds are quite sensitive to substituent conformations and configurations at sites quite remote from the carbonyl chromophore, and that this sensitivity can be understood in terms of chirality being communicated to the carbonyl chromophore via through-bond interactions. Bouman and Lightner[10] have employed theoretical calculations (based on the CNDO/S-MO model) in lending support to this hypothesis. It is, perhaps, significant that Bouman and Lightner[10] found that the orientation of the $n \rightarrow \pi^*$ electric dipole transition vector was extremely sensitive to substituent location and conformation, whereas the $n \rightarrow \pi^*$ magnetic dipole transition vector was relatively unaffected by substituent location. This latter result for carbonyl compounds is similar to our results for the N-nitrosopiperidine derivatives.

As was mentioned earlier, our results cannot be analyzed in terms of through-space versus through-bond effects and we cannot comment definitively upon the enhanced $n \rightarrow \pi^*$ rotatory strengths of the dimethyl derivatives. The only indication of through-bond effects in our calculations is the sensitivity of configurational mixing in the lowest excited state to substituent number and location. Although the lowest excited singlet state is calculated to be almost entirely $n\pi^*$ in all of the N-nitrosopiperidine structures varying amounts of another configuration is mixed in which involves a half-filled orbital delocalized throughout the 2p atomic orbital system of the ring carbons and substituent carbons. Although the presence of this configuration is slight (CI coefficient <0.02), it is possible that it has a decisive influence on the orientation of the $n \rightarrow \pi^*$ electric dipole transition vector.

Although *direct* calculational models of molecular chiroptical properties based on MO methods provide useful checks and tests of spectra-structure relationships such as sector rules, they seldom lead to well-defined relationships themselves. The purpose of the present study was to examine the validity of the simple sector rules proposed previously[1,5] for chiral nitrosamines and nitramines. Our results suggest that these sector rules do not have general applicability and must be used with a great deal of caution and circumspection. This conclusion is in agreement with observations made previously by Ripperger and Schreiber.[4] A more detailed account of the spectra-structure relationships appropriate for chiral nitrosamine and nitramine systems must await availability of very accurate wave functions for the nitrosoamino (NNO) and nitroamine (NNO_2) chromophores and an accurate representation for the interactions between these chromophoric units and the chiral fragments of the molecular systems.

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