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CIRCULAR DICHROISM OF NITRAMINES

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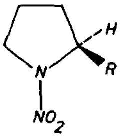
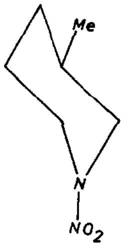
N-nitramines are substances of essential importance for theoretical studies in organic chemistry.[1] The nitramino group is a planar resonance hybrid with appreciable nitrogen-nitrogen double bond character.[2] The connected with planarity relatively high symetry of the nitroamino chromophore, makes this system a useful model for chiroptical studies.

In order to investigate these properties we synthesized several new optically active nitramines /1 - 4/. All these compounds were obtained by oxidation of the corresponding N-nitrosoamines with trifluoracetic acid in methylene chloride according to the Emmons method.[3] The presence of the nitramino group has been confirmed by IR spectra /all compounds exhibit 1510, 1330, 1240, 770 cm^{-1} bands characteristic of the N-NO$_2$ system[1]/ and elementary analysis.



1a R = CO$_2$Me

1b R = CH$_2$OH



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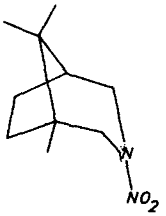

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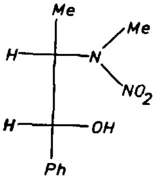

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The UV spectra of nitramines show a strong absorption band near 240 nm /e.g. N-nitropiperidine in methanolic solution has a maximum at 245 nm with ε 6500/. Stals et.al.,[4] assigned this band to the $^1B_2 \leftarrow {}^1A_1$ /$\pi \rightarrow \pi^*$/ + /$n\sigma \rightarrow \sigma^*$/ transition, basing on the VE.

SCF.CI calculations. Harris,[5] using the CNDO/s-CI method, attributed this intense absorption to the ${}^1B_2 \leftarrow {}^1A_1$ /$\pi_o \rightarrow \pi^*$/ excitation. He also predicted existence of the slightly lower energy forbidden ${}^1A_2 \leftarrow {}^1A_1$ /$n_o \rightarrow \pi^*$/ or ${}^1B_1 \leftarrow {}^1A_1$ /$\sigma \rightarrow \pi^*$/ transition which in the case of nitramines lies under the strong $\pi_o \rightarrow \pi^*$ absorption band and is therefore not observable.

This paper is concerned with the application of circular dichroism to the determination of the hidden bands position. The excitations with small electric but large magnetic transition moments, as have the $n \rightarrow \pi^*$ and other forbidden transitions, may appear stronger in the CD than in the UV spectrum.[6]

We have measured the CD spectra of our optically active nitramines. The aforementioned forbidden transition is optically active and visible in the CD spectrum near 270 nm /Table/.[7] The position of this band agrees with the energy of the ${}^1A_2 \leftarrow {}^1A_1$ /$n_o \rightarrow \pi^*$/ transition predicted by semiempirical calculations.[5] The N-nitramines exhibited the Cotton effect also at 240 nm, but strong absorption made measurements in this region difficult.

Table

Compound	M.p. °C B.p. °C	$[\alpha]_D^{25}$	CD[a/]	
			λ/nm/	[θ]
1a	52-53	-92.5 /c6,EtOH/	271	+1240
1b	168-170$_1$	-57.1 /c7,EtOH/	272	+3100
2	70-75$_1$	+8.3 /neat,l=1dm/	273	positive[b/]
3	140-141	+35.8 /c8,C_6H_6/	273	+ 500
4	67	+28.3 /c6,EtOH/	270	+ 910

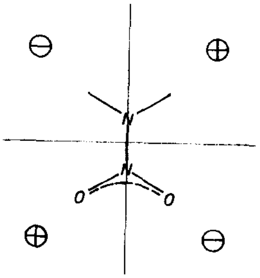
a/ measured in methanolic solution

b/ partially racemic sample

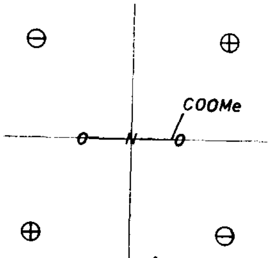
We were also interested in the correlation between the Cotton effect sign and the absolute configuration of these compounds. Owing to its planar arrangement, the nitramino chromophore has C_{2v} symmetry. The Schellman symmetry rules for optical rotation[8] predict that the Cotton effect sign for the C_{2v} point group is governed by the quadrant rule. However, detailed calculations of the C_{2v} symmetry chromophores decidedly show that the CD sign varies with the octants.[9] For this reason we propose the octant rule for correlation the CD sign with the absolute configuration of nitramines. The sectors are determined by the symmetry properties of the π^*/b_1/ orbital. The sector signs are opposite to those of the well- known rule for ketones.[10]

To test our rule we compared the CD of compounds 1 - 4, synthesized by us, with the Cotton effect sign predicted for them by this rule. It is obvious from the projections given below that N-nitro derivatives of /S/-alanine 1, d-camphidine 2 and /S/-β-pipecoline 3 in equatorial conformation would give a positive Cotton effect, this being in good agreement with our experimental results. The conformation of /α R, β S/-N-nitroephedrine 4 is difficult to establish and the CD sign is difficult to explain. These examples refer only to rear octants; nitramines with perturbing groups in the front octants would be rather difficult to obtain.

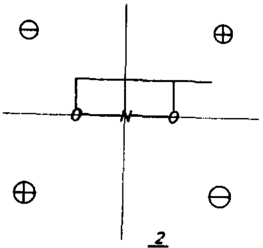
The sector rule for nitramines has been used to introduce a new sector rule for N-nitrosoamines.[11]



signs for upper sectors



1a



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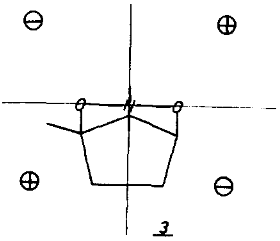

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References and Notes

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7. This CD band is completely solvent insensitive, e.g. 3 shows the maximum at 273 nm in MeOH, at 273 nm in acetonitrile, and at 272 nm in cyclohexane. However, in circular dichroism this apparent solvent insensitivity may result from the overlap with the adjacent strong $\pi_o \longrightarrow \pi^*$ band. Delocalization of the n_o orbital, which is in fact of π character, can also decrease the solvent sensitivity of these band.
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