Tetrahedron. Vol. 32, pp. 847 to 853 Pergamon Press 1976. Printed in Great Britain

OPTICAL ACTIVITY OF NITROSAMINES
A NEW SECTOR RULE FOR THE N-NITROSO CHROMOPHORE

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(*Received in UK* 18 *August* 1975; *Accepted for publication* 20 *October* 1975)

Abstract—We have reinvestigated the chiroptical properties of the nitrosamines as ambiguous statements have been reported in the literature.

The present paper reports a new sector rule for the N-nitroso chromophore, which has been developed through perturbation of the octant rule for the higher symmetry N-nitro chromophore. The "lowered symmetry" sector rule so obtained has been tested on several nitrosamines of known conformation and on compounds occurring in equilibrium mixtures of conformational isomers. The conformation of the former and the *syn/anti* rotamer ratio of the latter were determined by NMR spectroscopy. The sign of the Cotton effect of the nitrosamines investigated by us and of those reported in the literature is governed by the rule here presented.

The vibrational structure of the CD spectra has been discussed.

The N-nitrosamino group is a planar resonance hybrid with a N–N bond of partial double character.[1] The consequent hindered rotation about the N–N bond makes this system a good model for stereochemical studies. It is particularly suited for chiroptical measurements on account of the rigid orientation of the chromophore with respect to its asymmetry and weak long wavelength absorption. Since the N-nitroso group can easily be introduced into secondary amines, it should be possible to assign the absolute configuration of amines simply by applying the rules correlating the sign of the Cotton effect with the configuration of the nitrosamines.[2] The N-nitrosamine sector rule suggested by Snatzke *et al.*[3] (Fig. 1) was based on the nodal properties of the orbitals involved in the $n_N \rightarrow \pi^*$ transition attributed by them to the longer wavelength absorption band. They[3] determined the sector signs empirically on the basis of the sign of the Cotton effect for N-nitrosopipecoline (**1**) which was used as a model compound and assumed to be of equatorial conformation which is the most stable. Harris and Spragg[4] concluded from the NMR spectrum of **1** that the Me group of this compound is primarily axial. Based on this assumption and on the CD studies of N-nitroso-imino acids, Gaffield *et al.*[5] suggested that the sector signs should be reversed in relation to those of the original rule. Beyerman *et al.*[6] disagreed with this suggestion based on the interpretation of the chiroptical data of **1** and (R,R)-N-nitroso-*trans*-2,6-dimethylpiperidine (**2**). Ripperger and Schreiber,[7] after studying the CD of about thirty nitrosamines, concluded that as application of the sector rule only provided ambiguous information regarding their absolute configuration of the nitrosamines; they compared the CD sign of these compounds with the sign of the Cotton effect for nitrosamines which are similar in structure and have a known configuration. Owing to the conflicting statements in the literature we reinvestigated the problem.

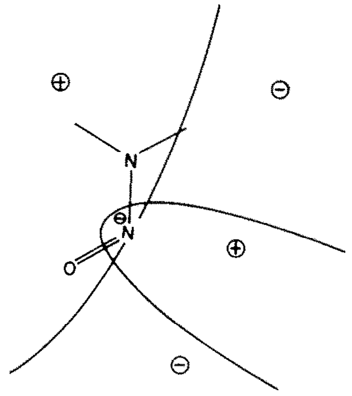
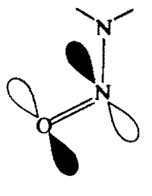


Fig. 1. Sector rule for the nitrosamino chromophore proposed by Snatzke *et al.*[3] Signs are referred for upper sectors.

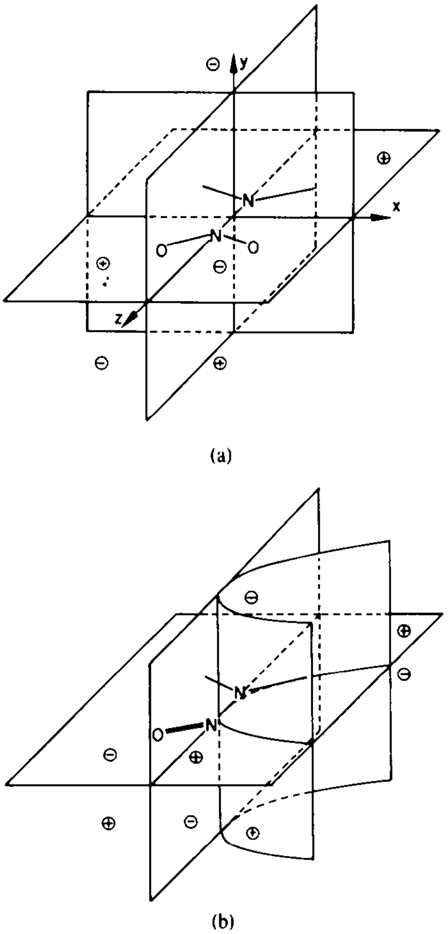
Nitrosamines exhibit a weak, long wavelength absorption band near 370 nm corresponding to $n_a \rightarrow \pi^*$ ($A'' \leftarrow A'$) transition,[8] where n_a is an antisymmetric linear combination of the p atomic orbitals of nitrogen and oxygen. Such a structure of orbitals involved in lowest energy transition has been confirmed by Rabalais *et al.*[9] with the aid of photoelectron spectroscopy (PES).



Snatzke *et al.*[3] localized the nonbonding orbital on the N atom with nodal properties differing from those of the n_a orbital, an assumption likely to lead to erroneous designation of the sectors. Moreover, the nodal planes of molecular orbitals do not always assign the sector rule for optical rotation. Since reversal of the sector signs cannot give satisfactory results in this situation, better sectors need to be designated.

Owing to its planar arrangement, the nitrosamino group belongs to the C_s point group. Schellmann's symmetry rules for optical rotation[10] predict for chromophores with local C_s symmetry a simple planar rule, and as nodal plane that of the π system in case of the nitrosamino chromophore. This suggestion does not allow for any differences in the chiroptical properties of the geometric nitrosamine isomers and is therefore inconsistent with experimental facts, as shall be demonstrated. Schellmann's paper[10] reports only "minimal requirements for each of the chromophores,"[10,11] whereas an actual sector rule can be more complicated.

Recently, Weigang[12] has worked out a "lowered symmetry model" for circular dichroism which recognizes that the electronic symmetry of a chromophore may be in fact higher than its nuclear symmetry. The sector rule for a given system can be obtained by applying a modification of the higher symmetry parent chromophore, using double perturbation techniques, in accordance with Weigang to derive a "lowered symmetry" rule for lactams from the carboxylate ion octant rule.[12] We started from the N-nitramine octant rule which we had previously elaborated (for nitramine lowest energy transition).[13] Formal removal of oxygen from the "parent" nitramino chromophore gives rise to the nitrosamino system. In this imaginary process the symmetry of the parent chromophore is lowered from C_{2v} to C_s. We assumed that the strong static coupling perturbation, induced in this way, brings about distortion of the nodal plane XY (Fig. 2), while the XZ and YZ planes remain planar. This procedure differs somewhat from that followed by Weigang, inasmuch as in his model it is the YZ plane that undergoes perturbation. But Weigang was dealing with weak perturbations, while transformation of the nitramino into the nitrosamino group must be regarded as a very strong perturbation.



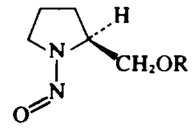
(a)

(b)

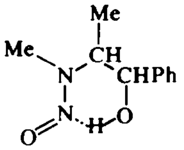
Fig. 2. (a) Octant rule for nitramines lowest energy transition.[13] (b) The "lowered symmetry" sector rule for the nitrosamino chromophore $n_a \rightarrow \pi^*$ transition.

The degree of nodal plane distortion has to be determined empirically. We have hypothesized that the XY surface passes through the C_α-carbon atom. The correctness of this option will be demonstrated experimentally.

To test our rule we measured the CD spectra of several nitrosamines (Table 1). We were particularly interested in compounds with fixed *syn*- or *anti*-conformation. We expected the N-nitroso derivatives of β-hydroxyamines, such as (S)-prolinole (**3a**) and (αR,βS)-ephedrine (**4**), to form 6-membered rings with intramolecular H-bonds stabilizing the *anti*-stereoisomers.



3a: R = H
b: R = Me



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Several authors[14,15] have suggested the presence of a 7-membered ring with H-bonding to the O atom in nitrosamino acids. The simple MO method shows, however, that the highest occupied molecular orbital (HOMO) is a nonbonding orbital with the largest amplitude on the more weakly electronegative N atom, since n_a is formed in the antibonding way.[16] It is therefore the N atom that takes part in the H-bonding, in accordance with the frontier orbital method.[17] This bond, however, should be weak, considering delocalization of the n_a orbital.

The IR spectra of **3a** and **4** have ν_{max} (CCl_4) near 3400 cm^{-1} for OH stretching which are independent of concentration, in agreement with the presence of intramolecular H-bonding. Compound **3a** and its O-Me derivative (**3b**) shows an N=O stretching band at the same frequency (1450 cm^{-1}). This is not in agreement with the 7-member ring hypothesis,[14,15] since in this case the N=O stretching of **3a** should appear at lower frequency.

NMR spectroscopy provides a powerful tool for establishing the conformation of nitrosamines. The relatively high energy barrier to rotation (23–29 kcal/mole)[18] about the N–N bond of the nitrosamine group, gives rise to the different chemical shifts for the *syn*- and *anti*-α-protons.[4,18,19] The magnetic anisotropy of the N-nitroso group can be explained in terms of NNO shielding cones and deshielding zones.[20] The *anti*-α-hydrogens will therefore resonate further downfield (by about 1 ppm) than the *syn*-α-hydrogens for the nitrosamines discussed in this paper. The NMR spectrum of **4** in $CDCl_3$ (Fig. 3) shows only one N–Me proton signal at 2·74 ppm and an α-methine signal at 4·6 ppm centered further downfield by 1·9 ppm. Similarly **3a** has an α-methine multiplet at 3·8 ppm with integration for one proton and γ-methylene absorption at 3·5 ppm (2H). These spectra indicate that *anti*-conformation is preferred in the case of β-hydroxynitrosamines and confirms the presence of a 6-membered intramolecularly H-bonded form in these compounds.

As can be seen from the projections shown in Fig. 4, the hydroxymethyl group of **3a** should give a positive contribution to the Cotton effect sign, this being in accordance with the CD spectrum (Fig. 5).

Another example of a nitrosamine with fixed conformation is N-nitroso-*trans*-decahydroquinoline (**5**) occurring only in the *anti*-conformation[7,21] owing to the steric

Table 1. Circular dichroism and absorption spectra of some nitrosamines (λ in nm, $[\theta]$ in deg. mole^{-1} cm^2)

Compound	UV /cyclohexane/[a]		CD /cyclohexane/[a]		CD /methanol/	
	λ	ε	λ	$[\theta]$	λ	$[\theta]$
3a	384	81	393	+170	384	+174
	370	102	378	-940	340	-1540
	358	89sh[b]	364	-1130		
			353	-840sh		
3b	385	98	388	+610	385	+193
	370	120	373	+350	331	-1300
	359	89sh	365	-20		
			358	+79		
			351	-20		
			345	+13		
4	376	99sh	374	+1890sh	354	+1530
	364	117	363	+2150		
	352	92sh	350	+1500		
5	382	84	375	-2830	346	-2460
	369	83	364	-2730		
	357	62sh				
	345	40sh				
6	384	95	376	+1410	370	+550sh
	371	116	364	+1670	351	+910sh
	359	100	355	+1340sh	345	+1030
	345	73sh				
7					382	-236
					368	+340sh
					354	+1020sh
					343	+1310
8[c]	377	108	375	+650	345	+680
	365	115	362	+750		
	364	84	349	+660sh		
	342	50sh				
9	380	102	374	+1090	346	+890
	368	119	362	+1210		
	357	93	352	+900		
	346	60sh				
10	383	63	385	+1660	380	+960sh
	370	79	372	+1900	365	+1760sh
	358	60sh	358	+1300	354	+1980
	346	37sh	347	+740sh		

a/ Cyclohexane:dioxane /9:1/ was used as a solvent in case of 3a, 3b, 4, 6, and 7.

b/ sh = shoulder

c/ Data was corrected to the optical purity.

interaction of the N–NO group with the equatorial C-8 substituent.

The strong negative Cotton effect of (S)-5 is inconsistent with the sign predicted by the Snatzke sector rule.[3,7] The CD sign of 5 is satisfactorily explained by our rule, as can be seen from the projection shown in Fig. 4.

Compound 2 also exists in one conformation in which the Me group *cis* to the nitroso group is axial, the other Me group being equatorial as is evident from the NMR spectrum.[4] The sector projection of 2 (Fig. 5) shows the axial Me group in the positive sector and the equatorial group in the nodal plane. The CD spectrum of 2 measured by Beyerman[6b] exhibits a strong positive Cotton effect ($[\theta] = +9 \times 10^3$) as expected from the aforementioned projection.

Most nitrosamines occur as equilibrium mixtures of

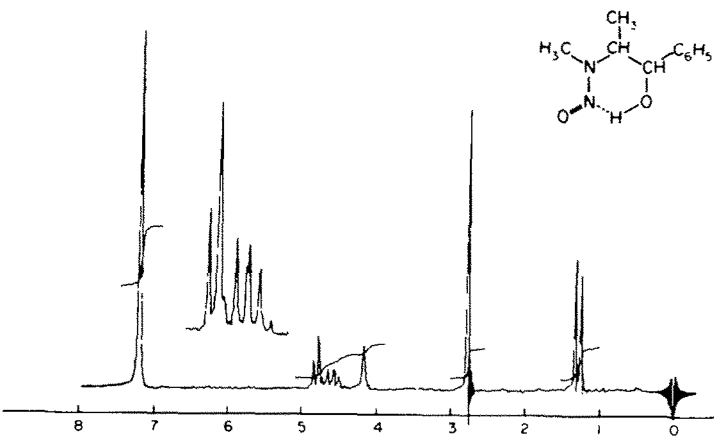


Fig. 3. The 80 MHz PMR spectrum of (αR,βS)-N-nitrosoephedrine (4) in CDCl$_3$ solution.

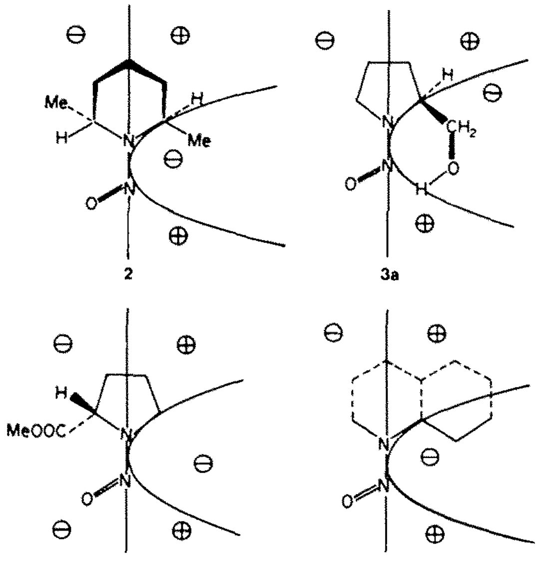


Fig. 4. "Lowered symmetry" sector rule projections of **2**, **3a**, **5** and **6**. Signs are referred for upper sectors.

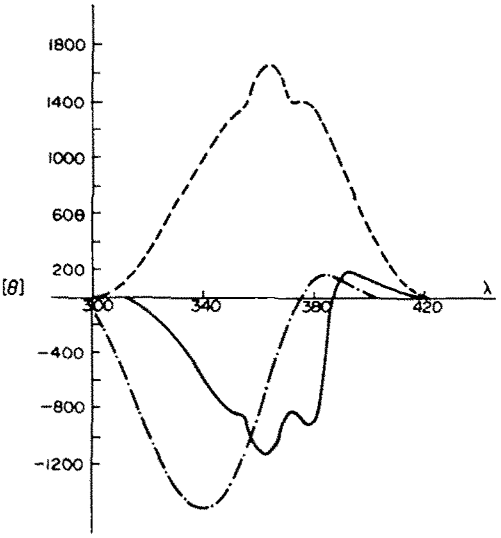
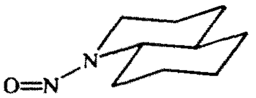


Fig. 5. CD spectra of (S)-N-nitrosoprolinole (**3a**) in methanol (–·–·–·–), in cyclohexane:dioxane (9:1) (———) and (S)-N-nitrosoproline methyl ester (**6**) in methanol (-----).



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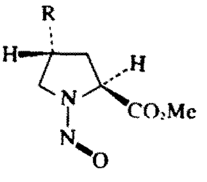
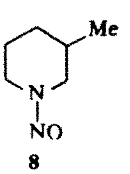


6: R = H
7: R = OH

syn- and *anti*-isomers. The ratio of these rotamers can easily be assigned by NMR spectroscopy. Lijinsky *et al.*[14] have shown that (S)-N-nitroso-proline occurs mainly in the *syn*-conformation and found the intramolecular H-bond to be responsible for the preponderance of this form. It is evident from the NMR spectra in CDCl$_3$ that also the *syn*-rotamer is more abundant in equilibrium mixtures of (S)-N-nitroso-proline methyl ester (**6**) and (αS,βR)-N-nitroso-hydroxyproline methyl ester (**7**). The predominance of the *syn*-conformer in these compounds in solution is caused by electrostatic interaction between the NNO and the carboxyl or ester groups. Compound **6** illustrates the essential importance of the influence of the conformational state on the CD sign of nitrosamines. The sector rule presented by us predicts a positive sign of the Cotton effect for **6** in the *syn*-conformation, in contrast to the sign of that effect for the analogous compound **3a** occurring in *anti*-conformation. The Cotton effect for **7** is stronger than that for **6**. Projection of **7** shows an additional positive contribution of the OH group to the CD.



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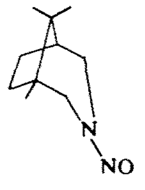

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Some of the nitrosamines, as (S)-N-nitroso-β-pipecoline (**8**) or N-nitroso-d-camphidine (**9**) occur as equimolar mixtures of *syn*- and *anti*-rotamers.[18,22] According to earlier rules,[3,5] the molecular ellipticity of such compounds should equal or approximate zero, because the dissymmetrically placed groups lie in sectors with different signs for each of the conformations. This is not in agreement with experimental facts, since both **8** and **9** exhibit CD curves of appreciable ellipticity. It is evident from the projections given in Fig. 6 that the sign of the Cotton effect for these compounds is governed by our "lowered symmetry" rule, since the conformers of **8** and **9** give both the same CD sign.

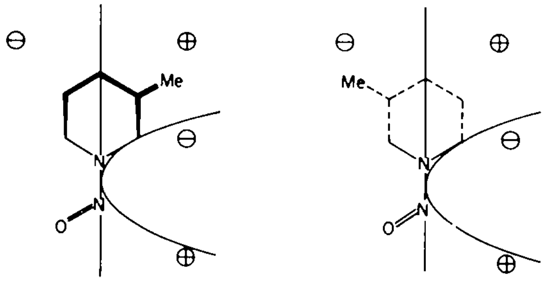

Fig. 6. Projection drawing of (S)-nitroso-β-pipecoline (**7**) in *syn*- and *anti*-conformation.

Another advantage offered by the rule suggested by us, as compared with earlier rules, is that skeletons and groups placed symmetrically towards the XY plane can be left out of consideration, thus simplifying practical analysis of the Cotton effects and reducing the ambiguity of stereochemical determinations. While consideration of the CD sign for **1** formerly[1,5,6] called for a complex analysis of the contribution of piperidine ring atoms, the rule suggested by us requires only consideration of the contribution made by the group†

By means of this rule it is possible to predict the correct CD signs for a number of other nitrosamines (e.g. the N-nitroso derivatives of amino acids,[5] piperidines,[1,6,7] and naturally occurring amines[7]), but the restricted length of this paper does not permit a detailed discussion of this problem.

The CD curves of **7**, **3a** and its O-Me derivative **3b** change in sign in the long wavelength side (Figs. 4 and 7). This reversal of sign can be regarded as evidence of at least two overlapping Cotton effects of opposite sign. A simple explanation is that there are two species present. Coulombeau and Rassat[21a] and Djerassi *et al.*[21b] assumed that reversal of the sign was due to solvated and nonsolvated forms existing in equilibrium, even in the case of rigid bicyclic ketones in cyclohexane solution. The CD associated with either the solvated or the nonsolvated species could have the same or the opposite sign depending on the chirality of their respective solvent cages. This explanation seems unsatisfactory. For a criticism of this viewpoint see Ref. 24.

An alternative explanation is provided by consideration of the vibrational effects. A symmetric chromophore becomes optically active owing to the perturbation which is brought about by its asymmetric environment[12,25] and causes the "allowed character" of the rotational strength.[26] Molecular vibrations undergo coupling to electronic states and affect strongly the CD curve.[26,27] The rotatory strength produced by totally symmetric vibrations also occurs in the absence of vibrational coupling, whereas nontotally symmetric vibrations produce rotational strength of "forbidden character",[26] the sign of which may differ from that of the rotational strength "allowed". The sign reversal observed in CD can be explained by progression in the two vibronic modes which produce the aforementioned "characters". In the case of **3b**, which shows in cyclohexane a CD curve typical for vibronic coupling (Fig. 7), the solvent effect on the CD probably is not related only to vibrational effects, but also to conformational changes in the polar and flexible side chain.

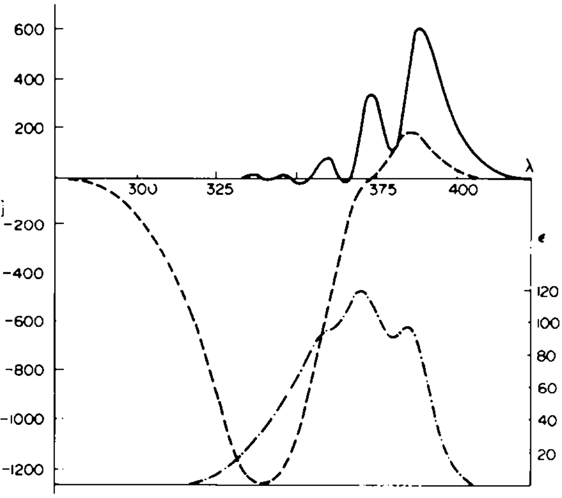

Fig. 7. CD spectra of (S)-N-nitroso-O-methylprolinole (**3b**) in methanol (-----) and cyclohexane:dioxane (9:1) (———) and UV spectrum of **3b** in cyclohexane:dioxane (9:1) (-·-·-·-).

The vibrational structure of the nitrosamine CD spectra is more pronounced in cyclohexane than in methanolic solution. The sharpness of the vibrational structure of the CD curves is enhanced in comparison with that of the absorption spectra (Fig. 7), an effect which is characteristic of vibrational coupling.[28] We have attributed the absorption band, the shape and position of which is the same for all nitrosamines as a "pure forbidden" component. The "pure allowed" component can be ascribed to the CD bands of **4**, **8**, **9** or (S)-N-nitroso-N-benzyl-α-methylbenzylamine (**10**). Whenever a transition is strongly electric dipole forbidden and magnetic dipole allowed, as in the case of nitrosamine $n_a \rightarrow \pi^*$ transition, the chromophore can be characterized under the so-called Case II of Moffit and Moscowitz.[29] In this case the absence of correspondence between the CD and the UV band contours can be explained. The "forbidden character" in the CD of **3a** and **7** can be assigned to the hot band (transition from the excited electronic state[30]), which appears as the longest wavelength CD subband. However, this assumption is tentative and requires further study, e.g. temperature dependence measurements. The "allowed character" points to the influence of the asymmetric perturbation of the chromophore and can be analysed using the sector rules. Since the molecular constants of the nitrosamine molecules studied by us are unknown, further discussion of vibrational coupling would be premature.

In conclusion, the "lowered symmetry" sector rule for

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†A projection of the conformations of compound (R)-**1** (Δε = + 0·65)[5] would show the Me group in the *syn*- and *anti*-axial conformation to lie in positive sectors, while the *anti*-equatorial conformation would be seen to lie in the nodal plane.

nitrosamines can be obtained from the nitramine octant rule by the perturbation method. The sector rule developed by us can successfully be used for determining the correct sign of the Cotton effect of a variety of nitrosamines, also where earlier rules have failed. That is why this new nitrosamine sector rule can also serve as a basis for assigning the absolute configuration of parent amines.

Sign reversal in the CD curves of several nitrosamines can be explained as resulting from vibronic coupling.

EXPERIMENTAL

CD measurements were performed at room temp. on a JASCO J-20 spectropolarimeter, cell length 10 mm, concentration varying from 1 mg/ml to 4 mg/ml. UV spectra were recorded on a Specord UV-VIS spectrophotometer. NMR spectra were measured on a Tesla BS-487 instrument operating at 80 MHz. The nitrosamines were prepared by nitrosation of the parent amine with nitric acid prepared *in situ.*[31]

(S)-N-*nitrosoprolinole* (**3a**). Oil; $[\alpha]_D^{25}$ $-138°$ (c 4, EtOH); NMR (δ, $CDCl_3$): 4·4 (m, 1H, *anti*-$C_\alpha H$), 3·95 (s, 1H, $CH_2O\underline{H}$), 3·88 (m, 2H, $C\underline{H}_2OH$), 3·55 (m, 2H, $C_\delta H_2$), 2·05 (m, 4H, $C_\beta H_2C_\gamma H_2$); IR (10% in $CHCl_3$): 3410 (br, OH), 1460, 1415, 1310; IR (0·05% in CCl_4): 3420 (br, OH); (Found: N, 21·12. $C_5H_{10}N_2O_2$ requires: N, 21·52%).

(S)-N-*nitroso*-O-*methylprolinole* (**3b**). **3** (0·007 mole) was dissolved in N,N-dimethylformamide (10 ml), then BaO (3·0 g) and MeI (2·5 ml) was added. The mixture was stirred overnight, poured into water and extracted twice with ether (30 ml). The ethereal layer was dried over $MgSO_4$, evaporated and distilled; b.p. 132–135$^\circ_2$; $[\alpha]_D^{25}$ $-81·5°$ (neat, $l = 0·5$ dm); NMR (δ, $CDCl_3$): 4·56 (m, 0·8H, *anti*-$C_\alpha H$), 4·3 (m, 0·4H, *anti*-$C_\delta H_2$), 3·69 (d, 1·7H, *anti*-$C\underline{H}_2OMe$), 3·5 (complex, 1·9H), 3·28 (s, 0·75H, *anti*-OMe), 3·19 (s, 0·25H, *syn*-OMe), 2·0 (m, 4H, $C_\beta H_2$–$C_\gamma H_2$); IR (1% in $CHCl_3$): 1460, 1415, 1320; (Found: N, 19·49. $C_6H_{12}N_2O_2$ requires: N, 19·43%).

(αR,βS)-N-*nitrosoephedrine* (**4**); m.p. 90–91°, $[\alpha]_D^{25}$ $+45·5°$ (c 2·5, MeOH), (lit.[12] m.p. 93–94°); NMR (δ, $CDCl_3$): 7·23 (s, 5H, ArH), 4·6 (complex, 2H, ArC$\underline{H}$–C$\underline{H}$), 4·13 (s, 1H, OH), 2·73 (s, 3H, NCH_3), 1·25 (d, 3H, $CHC\underline{H}_3$); IR (10% in $CHCl_3$): 3390 (br, OH); IR (0·1% in CCl_4): 3400 (br, OH).

(aS)-N-*nitroso-trans-decahydroquinoline* (**5**); amorphous, m.p. 47–50°, $[\alpha]_D^{25}$ $-188°$ (c 5, EtOH), (lit.[21] 52–56°; $[\alpha]_D^{20}$ $-229·6°$ (c 3·61).

(S)-N-*nitrosoproline methyl ester* (**6**); S-proline methyl ester hydrochloride (0·025 mole, 4·1 g) was dissolved in MeOH (50 ml), $NaNO_2$ (0·035 mole; 2·5 g) and conc HCl (0·5 ml) was added. The mixture was stirred for 2 hr at room temp. MeOH was evaporated and the residue triturated with EtOAc, the organic phase was evaporated to dryness and the residue destilled; yield 3·0 g (83%); b.p. 118–121°; $[\alpha]_D^{25}$ $-146°$ (c 5, dioxane); (lit.[7] b.p. 160$^\circ_{20}$; $[\alpha]_D$ $-112·2°$ (dioxane)); NMR (δ, $CDCl_3$): 5·19 (q, 0·63H, *anti*-$C_\alpha H$), 4·3 (complex, 1·8H, *anti*-$C_\delta H_2$ + *syn*-$C_\alpha H$), 3·69 (s, 1·08H, *anti*-CO_2CH_3), 3·57 (s, 1·92H, *syn*-CO_2CH_3), 3·6 (m, *syn*-$C_\delta H_2$), 2·2 (complex, 4H, $C_\beta H_2C_\gamma H_2$).

(αS,γR)-N-*nitrosohydroxyproline methyl ester* (**7**); obtained analogously to **6** as oil; $[\alpha]_D^{25}$ $-131°$ (c 3·8, EtOH); NMR (δ, $CDCl_3$): 5·25 (t, 0·27H, *anti*-$C_\alpha H$), 4·4 (complex, 1·5H, *anti*-$C_\delta H_2$ + *syn*-$C_\alpha H$), 4·2 (m, 1H, $C_\gamma \underline{H}OH$), 3·75 (s, 1H, OH), 3·72 (s, 0·8H, *anti*-CO_2CH_3), 3·62 (s, 2·2H, *syn*-CO_2CH_3), 3·7 (m, 1·4H, *syn*-$C_\delta H_2$), 2·2 (m, 2H, $C_\beta H_2$); (Found: N, 15·74; H, 5·92. $C_6H_{10}N_2O_4$ requires: N, 16·05; H, 5·79%).

(S)-N-*nitroso*-β-*pipecoline* (**8**); b.p. 56–60$^\circ_1$, $[\alpha]_D^{25}$ $+13·6°$ (c 5, dioxane); (lit.[34] b.p. 97–101$^\circ_{10}$, $[\alpha]_D^{20}$ $-57·2°$ (c 8·10, dioxane) for (R)-form.

N-*nitroso-d-camphidine* (**9**); m.p. 165–167°, $[\alpha]_D^{25}$ $+67·7°$ (c 7, dioxane); (lit.[31] m.p. 166·5–167°; lit.[33] m.p. 167–170°, $[\alpha]_D^{18}$ $+74·9°$ (c 1·08, dioxane).

(S)-N-*nitroso*-N-*benzyl*-α-*methylbenzylamine* (**10**); oil; $[\alpha]_D^{25}$ $-42·6°$ (c 3, MeOH); NMR (δ, $CDCl_3$): 7·2–6·8 (complex, 10H, ArH), 6·12 (q, 0·36H, J = 7 Hz, *syn*-$ArCHCH_3$); 5·30 (q, 2·6H, *anti*-$ArCHCH_3$, J = 7 Hz), 5·15 and 4·60 (AB system, 0·25H, *anti*-$ArC\underline{H}_2$, J = 14 Hz), 4·88 and 4·02 (AB system, 1·8H, *syn*-$ArCH_2$, J = 14 Hz), 1·71 (d, 2·6H, *anti*-$ArCHCH_3$, J = 7 Hz), 1·10 (d, 0·4H, *syn*-$ArCHC\underline{H}_3$, J = 7 Hz).

Acknowledgements—The authors wish to express their appreciation to Prof. O. E. Weigang, Jr. (Tulane University, New Orleans) for helpful discussion. Furthermore we thank Dr. T. Sokołowska for reading the manuscript of this paper, Miss E. Gwizdała for the CD measurements and Mr. A. Kunikowski for assistance in UV measurements.

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