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NMR BENZENE SOLVENT SHIFTS OF αβ UNSATURATED ALDOXIMES AND KETOXIMES.

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Oximes of αβ unsaturated carbonyl compounds, prepared by known or modified methods present in general (1,2), a mixture of syn and anti isomers (respectively cis and trans to the double bond). Carbonyl compounds substituted in α seem to yield only the anti form (3). As a rule, the s-trans conformation is retained in the corresponding oximes. The attribution of the two vinyl systems was based on the well known deshielding of nearby protons by the hydroxyimino group (4). NMR spectra obtained with a VARIAN HA 60 spectrometer at room temperature (about 10% solutions, TMS internal reference, exactitude superior to 0.05 ppm) were analyzed, when needed, on an IBM 1130 computer (1).

Acrolein oxime exists as a single s-trans anti form, in accordance with the theoretical calculations of LEIBOVICI (5). The NMR spectrum of methyl vinyl ketoxime in CCl_4 shows a syn/anti ratio of about one to three (Fig. 1). Due to NOH anisotropy, proton "C" shows a relative downfield shift of about 0.75 ppm when going from anti to syn isomer. Comparison of analyzed spectra yielded the results given in Table 1. Positive and negative values, given in cps, correspond respectively to upfield and downfield shifts between CCl_4 and C_6D_6 solutions. The observed effects are consistent with a specific interaction between benzene and unshared electron pairs on nitrogen and oxygen atoms of the oxime. It is noteworthy that little change is observed when passing from a syn to anti form: the resulting ASIS*) center of anisotropy is located near the bisector plane of the hydroxyimino group positions. The relative shifts of methyl vinyl ketoxime present a linear variation with the mole fraction of benzene added to tetrachloride solution, commonly accepted as proof for the formation of an equimolar "complex " between solvent and solute (6). Yet, identical opposite variations are observed by *dilution of the benzene solution with an inert solvent like* CCl_4. The "complex" would therefore be very weak, its energy not exceeding that of Van der Waals' interactions. The ASIS recorded by NMR gives only time-averaged values resulting from very rapid processes of formation and break-down of favorably oriented groups of one solute and one or more solvent molecules, drawn at random from the medium. Such a model seems more acceptable than a 1:1 complex (7). Still, the effect of these interactions may be considered as a statistical result of a single center of anisotropy.

It is with this in mind that we have managed to determine the relative positions of benzene and oxime. We have used JOHNSON and BOVEY'S values (8), attributed to ring currents, neglecting the isotopic effect of benzene D_6.

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*) ASIS - Aromatic Solvent Induced Shift.

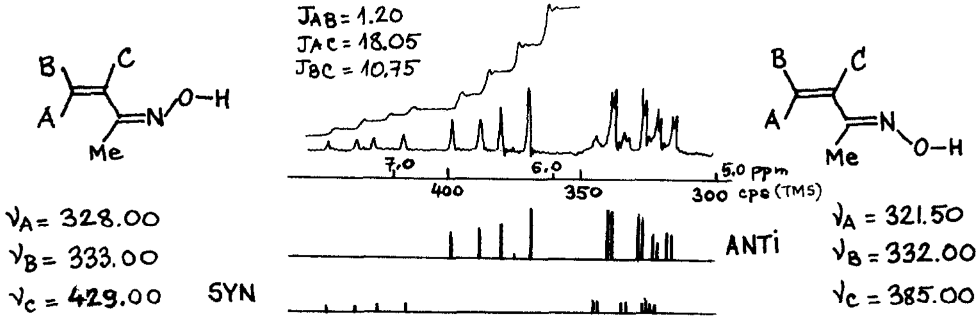
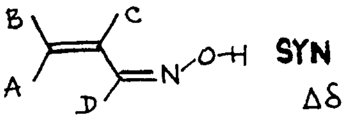
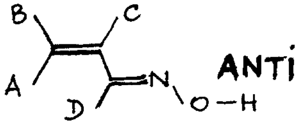


Fig. 1

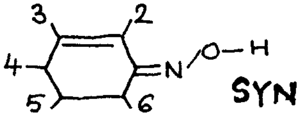
TABLE 1

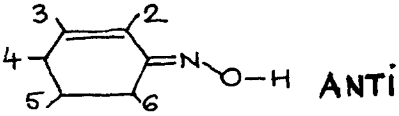


$\Delta\delta = \nu_{CCl_4} - \nu_{C_6D_6}$ (cps)



OXIME	ISOMER	A	B	C	D	
ACROLEIN	ANTI	+23	+25	+2	+4	
α METHYL ACROLEIN	ANTI	+15	+15	CH_3+4	-3	
METHYL-2-BUTENE-1-ONE-3	ANTI	+7	+6	CH_3+1	CH_3+4	
METHYL VINYL	SYN	+15	+15.5	-10	CH_3-8	
KETONE	ANTI	+14	+15.5	-7.5	CH_3-8	
ETHYL VINYL	SYN	+12.5	+16.5	-6	CH_2 0	CH_3 +3
KETONE	ANTI	+13.5	+16.5	-8	CH_2 0	CH_3 +3
PENTENE-2-ONE-4	SYN	+28	CH_3+21.5	-14	CH_3+2	
	ANTI	+23.5	CH_3+21	-13	CH_3+7	
TIGLIC ALDEHYDE	ANTI	+21	CH_3 +19	CH_3+4	-3	
METHYL 2- PENTENE-2-ONE-4	ANTI	+13	CH_3 +19	CH_3-4	0	
MESITYL OXIDE	SYN	CH_3+11	CH_3+14	-15	CH_3-1	
	ANTI	CH_3 0	CH_3+14	-15	CH_3-1	





OXIME	ISOMER	2	3	4	5	6
ISOPHORONE	SYN	-21	CH_3+19	+21	CH_3+12	-1
	ANTI	-14	CH_3+19	+21	CH_3+12	-7
4,4 DIMETHYL	SYN	-18	+20	CH_3+17	+16	+2
CYCLOHEXENONE	ANTI	-16	+18	CH_3+17	+17	-4

Five parameters are necessary to determine the relative stereochemistry of an interaction, only three on a plane (9). We have found the position of this plane of the oxime molecule to be that of Fig. 2. It is distant by 2.8, 3.5 or 4.2 Å (d= 2, 2.5 or 3 benzene radius units) from the center of the benzene molecule and tilted about 56^{0} to its plane (this angle corresponds to the most rectilinear projection of the zero-shielding surface on the plane of the oxime molecule). Thus the negative center of the oxime falls near the plane of the benzene molecule, lacking in electrons, and the positive center, located on the double bond or beyond, near its six-fold axis, rich in π electrons. All studied (linear and cyclic) oximes were located with good to excellent agreement on the planes (d=2.0, 2.5 or 3.0). Methyl vinyl ketoxime holds the following position on plane d=3.0 (anti isomer), Fig. 3. (all molecules were located as in-scale Dreiding models).

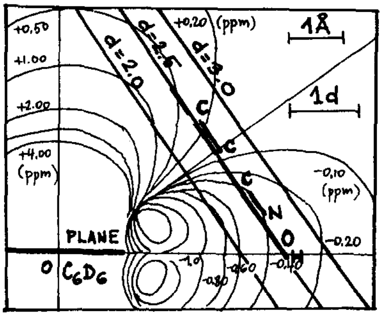


Fig. 2

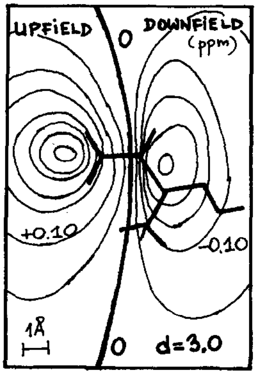


Fig. 3

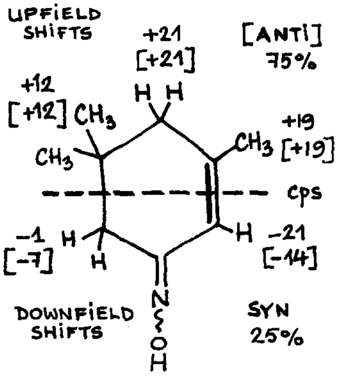


Fig. 4

In the case of mesityl oxide oxime, we find that the syn isomer retains the initial s-cis conformation, while the anti isomer accepts the sterically less hindered s-trans position, thus explaining different benzene shifts (Table 1) (1). As in the case of the parent carbonyl compounds (10), the unsaturated C=C bond does not affect the direction of the oxime dipole. The results allow in every case the direct deduction of a nodal surface drawn through the oxime molecule (Fig. 3) .(ex. Fig. 4, isophorone oxime), and separating upfield and downfield shift regions. Compared with the widely accepted nodal surface for carbonyl compound (11), this diagram suggests stronger benzene-oximino group than benzene-carbonyl group interactions.

By protonation of the oxime in benzene solution with CF_3COOH we expected to annihilate the ASIS by eliminating the mechanism of the repulsive interaction. Indeed, oxime protons with large upfield shifts give downfield protonation shifts, and vice-versa. Mesityl oxide oxime isomers are no exception (1). Nevertheless, similar effects result from dilution of the benzene solution with CCl_4 or $CDCl_3$: competitive Van der Waals' interactions on the solute explain the first case, added to competitive interactions of oxime and deuterium (in $CDCl_3$) with respect to benzene (12) in the second case.

Together with protonation of the oxime (presumably at the nitrogen lone pair) (13), they represent three independent manners of benzene-induced shift annihilation.

Beyond a 2-3 molar ratio of acid to oxime, variations become incoherent due to undefined interactions between oxime and CF_3COOH, which becomes solvent rather than additive.
In general, protonation shifts of oximes in benzene solution should be regarded with caution, while investigation of benzene-induced shifts alone offers obvious structural and stereochemical applications.

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