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^{13}C MAGNETIC RESONANCE SHIFTS OF α,β-UNSATURATED OXIMES, ALDEHYDES AND KETONES. CORRELATION WITH CNDO CALCULATIONS.

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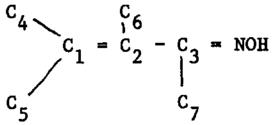
As part of a study on α,β -unsaturated oximes by spectroscopic and quantum chemical methods we have investigated their PMR characteristics (1)(2), ultraviolet and infrared absorption and performed theoretical calculations (3). The only reported ^{13}C NMR shift for an oxime is from LAUTERBUR (4), who found 33 ppm (CS_2 internal reference) for the imine carbon in methyl ethyl ketoxime. Together with the results of VINCENT and co-workers for thiazoles (5), this is also the only reported value in $R_2C=N-X$ systems. The $\delta^{13}C$ is 40.2 ppm for the trigonal carbon in thiazole itself, drastically shifted to 28.5 ppm when this carbon carries a methyl substituent.

We wish to present some of the ^{13}C data obtained for conjugated oximes, and relate them to configurational isomerism and electronic structure. The spectra were recorded at 25.1 MHz with total spin decoupling of natural abundance ^{13}C signals in pure liquids or saturated chloroform solutions. Fig. 1 represents the part of the spectrum covering the sp^2 carbons in crotonaldoxime: there is a set of signals for each of the two isomers. To our knowledge this represents the first case of differentiation of geometrical isomers at a trigonal nitrogen by CMR.
The assignments made are based on the spectra of the pure isomers and previous work in PMR (1)(2). The imine carbon (C_3) always resonates at lowest field, and is shifted by 5 ppm on methyl substitution. The increments induced by methyl substitution of the other carbons are very similar to those found in α,β-unsaturated aldehydes and ketones (6). The imine carbon resonates 42 ppm to higher field than in the corresponding carbonyl. Table 1 contains the ^{13}C shifts together with charge distribution in the conjugated oximes, obtained by the BJ-CNDO method (7) which has lead to successful calculations of ultraviolet absorption spectra and dipole mements of these molecules (3).
Fig. 2 represents the linear relationship between ^{13}C shifts and π charge for all sp^2 carbons: $\delta^{13}C(ppm) = 220\ Q_{\pi} - 165$ with a maximum deviation ± 0.022 on Q_{π}. The correlation with total electronic charges (on all s and p orbitals) Fig. 3 is of a somewhat better quality: $\delta^{13}C(ppm) = 126\ Q_{tot} - 440$ ($Q_{tot} \pm 0.04$). The magnetic shielding depends mainly on the local paramagnetic term (8) and numerous authors have found correlations between shifts and electronic densities on carbon (9), with a coefficient of 160-200 ppm per unit of charge.

The first attempt at the calculation of the electronic structure of acrolein was made by COULSON (10), and of methyl substituted acroleins by LUFT and BASSO (11) with the HMO-LCAO method. The PARISER-PARR-POPLE approximation (12) has been used by different authors for acrolein (13) and other α,β-unsaturated aldehydes and ketones (2) to successfully

Table 1. ^{13}C NMR chemical shifts (ppm from CS$_2$) of α,β-unsaturated oximes and BJ-CNDO and total charges.



	Oxime	C_1	C_2	C_3	C_4	C_5	C_6	C_7
×	acrolein	65.0	61.0	42.5	-	-	-	-
	s-trans E	0.9975	0.9894	0.9117	-	-	-	-
		4.0651	4.0181	3.8841	-	-	-	-
	α-methyl	72.0	55.0	41.0	-	-	176.5	-
●	acrolein	1.0560	0.9350	0.8870	-	-	-	-
	s-trans E	4.0760	3.9700	3.8340	-	-	-	-
▲	crotonal	55.5	73.0	42.5	174.5	-	-	-
	s-trans E	0.9493	1.0476	0.9050	1.0208	-	-	-
		4.0020	4.0590	3.8820	4.0500	-	-	-
△	crotonal	57.5	68.0	45.0	174.0	-	-	-
	s-trans Z	0.9522	1.0397	0.9073	-	-	-	-
		4.0087	4.0514	3.8838	4.0494	-	-	-
	methyl vinyl	75.5	59.5	37.5	-	-	-	184.5
■	ketone	1.0016	0.9880	0.8772	-	-	-	1.0124
	s-trans E	4.0710	4.0190	3.8320	-	-	-	4.0690

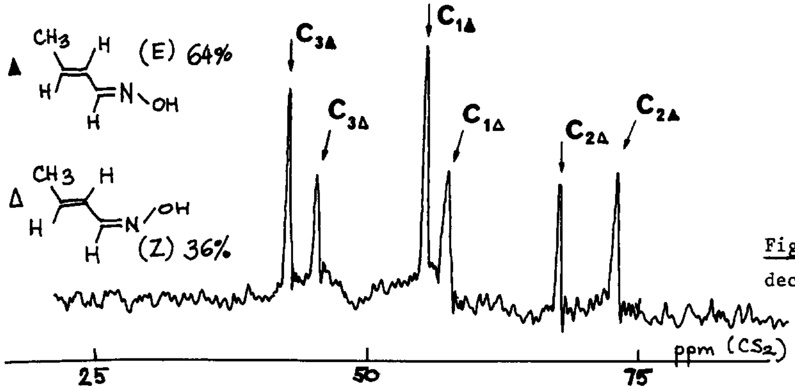


Fig. 1 ^{13}C total spin decoupled spectra of sp^2 carbons in crotonaldoxime isomers (CW, 200 scans, CDCl$_3$sol.)

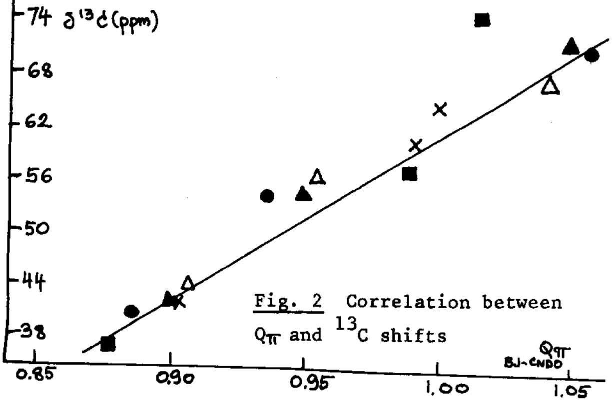


Fig. 2 Correlation between Qπ and ^{13}C shifts

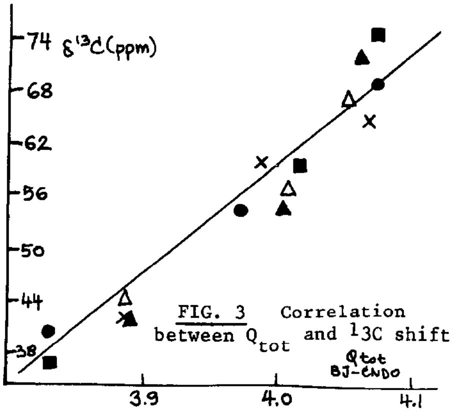


FIG. 3 Correlation between Q_{tot} and 13C shifts

Table 2. Q_π and Q_{tot} CNDO-2 charge densities, ^{13}C chemical shifts and dipole moments for **methyl-subsituted acroleins** (6) (16)

$C_1 = C_2 - C_3 = O$

	Compounds	Q_{C_1}	Q_{C_2}	Q_{C_3}	C_1	C_2	C_3(ppm)	μ cal(D)	μ obs(D)(16)
×	acrolein s-trans	1.0599 4.0006	1.0149 4.0370	0.8416 3.7575	56.8	56.4	0.4	2.68	3.11
●	crotonal s-trans	0.9214 3.9522	1.0531 4.0682	0.8425 3.7663	40.7	60.0	1.4	3.25	3.67
▲	tiglic ald. s-trans	0.9607 3.9764	1.0249 4.0239	0.8468 3.7730	45.2	53.5	0.0	2.84	3.39
■	methyl vinyl ketone s-trans	0.9596 4.0084	1.0040 4.0402	0.8319 3.7386	56.2(*)	65.1(*)	-4.4	2.91	3.16
					(*) inversed shifts - error in assignment (6)				
○	methyl isopropenyl ket. s-trans	1.0044 4.0320	0.9792 4.0020	0.8437 3.7578	68.5	49.2	-4.8	2.53	2.74
△	pentenone s-trans	0.9269 3.9585	1.0502 4.0725	0.8343 3.7491	50.0	60.3	-3.7	3.31	3.20
□	α-methyl pentenone s-trans	0.9709 3.9819	1.0200 4.0219	0.8332 3.7446	54.3	54.8	-5.2	3.04	3.20
♦	mesityl oxide s-cis	0.8618 3.8905	1.1234 4.1140	0.8062 3.7338	40.0	69.8	-3.4	2.50	2.84
◊	dimethyl pentenone s-trans	0.9143 3.9229	1.0850 4.0760	0.8394 3.7643	56.3	62.0	-8.9	2.43	2.88

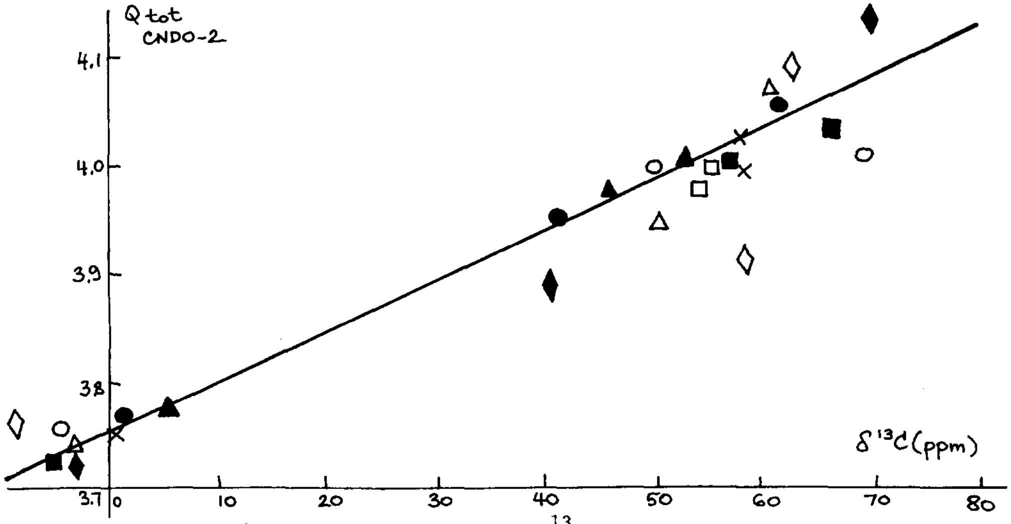


Fig. 4 Correlation between ^{13}C shifts and total charge densities Q_{tot}

calculate the energies of $\pi \rightarrow \pi^*$ transitions in the ultraviolet absorption spectrum and energies in the s-cis and s-trans conformations. We have used the CNDO-2 (σ,π) method (14), applied previously to acrolein (15), to determine the electronic structure of its methylated derivatives and correlate it with existing CMR data (6). Table 2 gives calculated π and total electron densities, ^{13}C shifts and dipole moments of the preferential planar conformations (16) of these compounds. The relationship between shifts and densities determined by the HUCKEL (11), PPP (2) or CNDO-2 methods is a rather parabolic one. Finally, a linear relationship (Fig. 4) is obtained when the total charge (in all s and p orbitals of carbon) is considered: $\delta\,^{13}C(ppm) = 220\,Q_{tot} - 830$, (± 0.1 on Q). Although the difference in electronic distribution between the s-cis and s-trans conformations of the carbonyl compounds is slight, the correlation is always better when the experimentally determined preferential conformation is considered (16). The data for dimethylpentenone (non-planar) and mesityl oxide correlate poorly, probably because of the inadequacy of the molecular geometries involved. When these cases are disregarded the maximum deviation of the relationship is reduced to ± 0.03 charge unit.

It is apparent that consideration of the $2p_z$ carbon orbitals (π charge) is insufficient to express CMR shifts in conjugated aldehydes and ketones, while inclusion of electronic distribution in other orbitals allows for satisfactory correlations (9).The effect is less visible in the corresponding oximes, presumabely because of the precision of a CNDO calculation on molecules containing both an oxygen and a nitrogen atom, and the approximate geometries used (3). However, the shift difference between oxime isomers may be related successfully to the modification in their electronic structure. Finally, CMR appears as an interesting complement to PMR techniques applied in structural organic chemistry.

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