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CMR DETERMINATION OF RESONANCE HYBRID WEIGHT CONTRIBUTIONS IN UNSATURATED MOLECULES.

ESTIMATION OF THE 1,4-DIPOLAR CONTRIBUTION IN CONJUGATIVELY UNSATURATED KETONES

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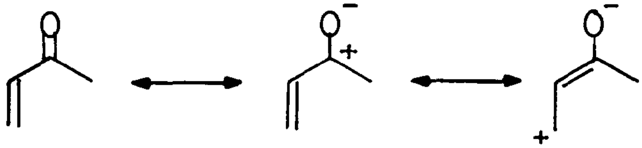
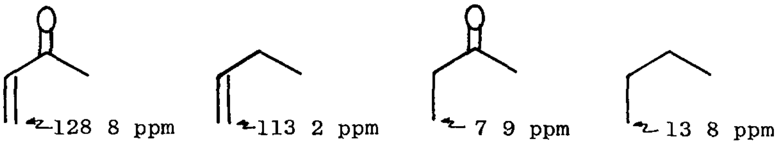
While cmr spectroscopy has been used to study charge distributions in many organic ions, its related application to neutral non-aromatic molecules has been much more limited We have recorded the cmr spectra of a variety of conjugated alkenones and with the aid of a few simple equations have been able to relate the observed chemical shifts to the relative contributions of valence-bond structures 1 - 3. The usefulness of such a procedure lies not only in its ability to provide a simply understood electronic description of the molecule and identify trends or anomalies, but also in its eventual application to the prediction of chemical reactivity Herein, we describe a method to determine Z, the relative weight contribution of hybrid 3.


1 2 3

We have measured the cmr shift difference between the signal for the β carbon atom in the alkenone and the resonance for the analogous carbon atom in the corresponding alkene. As it is known that cmr shifts are governed primarily by the paramagnetic shielding term,[1] this chemical shift difference can be largely ascribed to the variation in total (sigma plus pi) charge density between these two centers[2] In order to remove the sigma density component, we have determined the chemical shift difference between the β carbon atom signals in the corresponding alkanone and alkane Subtraction of this latter differential from the former should yield a value which is related to the pi electron deficiency at the β carbon atom in the enone A number of other investigators have found a strong correlation between cmr shifts and pi electron densities with values typically existing in the 160-200 ppm/pi electron range [5] Using an intermediate value of 180 ppm/pi electron[6] allows us to convert our former number into the fractional pi electron deficiency at the enone β carbon, which in the valence-bond formalism can be equated with $\underline{Z}$ Taking methyl vinyl ketone as an example, and using the chemical shifts indicated below, one obtains



$$\underline{Z} = [(128\ 8 - 113\ 2) - (7\ 9 - 13\ 8)]/180$$
$$= 0\ 12$$

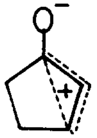
We have treated a number of enones in this manner, and the results are presented in Table I, along with the pertinent cmr data As can be seen, the weight contribution of hybrid $\underline{3}$ increases as one proceeds down the table, reflecting the expected abilities of the substituents to stabilize positive charge Where comparison is possible, our results are also in relative accord with the CNDO/2 pi charge densities calculated by Bertelli, et al [8] In order to further test our method, we have computed $\underline{Z}_\alpha$, wherein the above procedure is now applied to the α, instead of the β, carbon atom Since the electronic environment of this carbon remains essentially unchanged in hybrids $\underline{1}$ - $\underline{3}$, one would expect $\underline{Z}_\alpha$ to remain constant Indeed, for the compounds described in Table I, we find $\underline{Z}_\alpha = -0\ 08 \pm 0\ 03$ [9]

Having demonstrated the validity of our method, we have extended it to include compounds such as homoconjugated ketones, cyclopropyl ketones and annulenones The results of these studies and the questions they bear upon will be discussed at a later date

Table I CMR Shifts and Z Values [7]

Compound	alkenone[a]	alkene[b]	alkanone[c]	alkane[d]	Z	CNDO/2 π density[8]
p-benzoquinone	136.5	124 5	36 7	27 0	0 05	
but-3-yn-2-one	78 1	67 4	7 9	13 8	0 09	
cyclohept-2-enone	146 3	132.5	24 4	28 5	0 10	
but-3-en-2-one	128 8	113 2	7 9	13 8	0 12	0 045
acetophenone	128 5[e] 133 1[f]	128 2[e] 125 7[f]	28 5[e] 25 9[f]	33 2[e] 30 2[f]	0 12	
cyclohex-2-enone	150 5	127 3	27 1	27 0	0 13	0 069
trans-pent-3-en-2-one	143 5	123 6	17 4	22 4	0 14	0 070
4-methylpent-3-en-2-one	155 0	130 7	24 6	27 8	0 15	
cyclohepta-2,6-dienone	143 9	132 5[g]	24 4	28 5	0 17	0 130[h]
cyclopent-2-enone	164 9	130 7	23 2	25 9	0 21[i]	

[a] Shift of the β carbon atom. [b] Shift of the olefinic atom which corresponds to the β carbon atom in the enone [c] Shift of the β carbon atom [d] Shift of the atom which corresponds to the β carbon atom in the alkanone [e] ortho [f] para [g] Approximated using cycloheptene [h] The sum of both β positions in 4,4-dimethylcyclohexa-1,4-dienone [i] Several explanations are possible for this abnormally large value One which is currently under investigation involves viewing the bis-homocyclopropenone 1 as a substantial contributor to the cyclopent-2-enone ground state



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1 J B Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N Y , 1972, Chapter 4

2 Due to the difficulty in estimating the mean excitation energy (ΔE), most workers have assumed it to remain constant within a given series of compounds Their findings seem to support the validity of such an assumption[3] Furthermore, the cmr signal for the carbonyl carbon atom in ketene is located *ca* 10 ppm upfield from the carbonyl resonance in acetone[4] If ΔE factors were of determining import, one would have expected the ketene carbonyl absorption to have been displaced to much lower field due to the low lying π^* orbital in ketene We too have therefore assumed this term to remain relatively constant within the series of compounds investigated

3 See, for example, G E Maciel, *J Chem Phys* , **42**, 2746 (1965) and references therein

4 (a) J Firl and W Runge, *Angew Chem Int Ed* , **12**, 668 (1973)
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5 (a) P C Lauterbur, *ibid* , **83**, 1838 (1969), (b) H Spiesecke and W G Schneider, *Tetrahedron Lett* , 468 (1961), (c) E A LaLancette and R E Benson, *J Amer Chem Soc* , **87**, 1941 (1965), V Koptyug, A Rezvukhin, E Lippmaa and T Pehk, *Tetrahedron Lett* , 4009 (1968)

6 We stress that although we obtain an absolute value for Z, we prefer to consider the relative position of this number in comparison to those from other ketones In such an approach, errors caused by inaccuracies in parameters such as ppm/pi electron will tend to cancel

7 FT-cmr spectra were recorded on a Varian XL-100 spectrometer Samples were run as *ca* 0 5 M solutions in $CDCl_3$ All chemical shifts are reported in ppm downfield from TMS

8 D J Bertelli and T G Andrews, *J Amer Chem Soc* , **91**, 5280 (1969)

9 Actually, the Z_α values are even more compacted than indicated, aside from cyclopentenone and acetophenone, Z_α = -0 08 ± 0 01 Furthermore, there is no correlation between Z_α and Z_β, i e Z_α varies randomly within its limits The negative values of Z_α are in accord with theoretical calculations[8,10]

10 P V Alston and D D Schillady, *J Org Chem* , **39**, 3402 (1974)