

13C-1H spin-spin couplings in cyclic alpha-beta-unsaturated enones and their protonated derivatives. Measurements and quantum chemical calculations

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^{13}C — ^1H Spin-Spin Couplings in Cyclic α,β -Unsaturated Enones and their Protonated Derivatives. Measurements and Quantum Chemical Calculations

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Direct and long-range ^{13}C — ^1H coupling constants are presented for the enone moieties of cyclopent-2-enone, cyclohex-2-enone and their protonated derivatives. A correlation is given between the experimental values and the results of quantum chemical calculations (CNDO/2, INDO). The existing calculations are modified in order to improve the relationship between the calculated and experimental results.

INTRODUCTION

In recent years ^{13}C NMR has developed into a rather powerful technique in the study of carbonium ions. Chemical shifts have, on the whole, been used for this purpose, mainly because of the relatively simple relationships which seemed to exist between this parameter and phenomena^{1a} such as charge densities and bond orders. By now it has become clear, however, that these simple relationships are confined to simple problems such as π -charge densities in aromatic systems. In cases where atomic charges, as well as bond orders, are reallocated as a consequence of chemical rearrangements, the relationships may even be deceptively simple, making correlations between calculated and empirical results^{1b} particularly cumbersome.

Spin couplings have a distinct advantage over chemical shifts because the number of independently obtainable experimental couplings exceeds that of the shifts. With the exception of direct (one bond) interactions, ^{13}C — ^1H couplings have scarcely been used in the study of, for example, carbonium ions; with the advent of pulsed spectrometers, however, the practical feasibility of measuring long-range couplings has markedly increased.

In this study ^{13}C — ^1H coupling constants for the enone moieties of the model systems cyclopent-2-enone and cyclohex-2-enone are presented, as well as those of the protonated derivatives. These systems were selected because a number of the interesting features mentioned above are combined in these molecules, such as conjugation, strain and reallocation of atomic charges. CNDO/2- and INDO calculations are used to rationalize the experimental results; the influences of protonation and geometrical changes are treated separately. Certain changes are made in the quantum chemical calculations in order to improve the relationships between calculated and experimental re-

sults. This study will, at a later stage, be extended to substituted cyclopentenones, where non-classical interactions are feasible.

EXPERIMENTAL AND RESULTS

Cyclopent-2-enone and cyclohex-2-enone were purchased from Aldrich and were used without further purification. The protonated derivatives were obtained by slowly adding fluorosulphonic acid to the ketones at approximately -70°C ; the resulting ions were thermally stable up to 150°C .

The ^{13}C NMR spectra were obtained at ambient temperature in 5 mm sample tubes at 25.1 MHz with a Varian HA-100 spectrometer or in 10 mm sample tubes at 22.6 MHz with a Bruker HX-90R spectrometer. Both instruments were interfaced with a Digilab FTS-3 NMR Pulsing and Data System.

In general, spectral bandwidths of approximately 1500–2000 Hz were combined with a 32 K transform size, yielding a digital resolution of 0.10–0.15 Hz. The effective resolution was approximately 0.3–0.5 Hz for the neutral systems and c. 0.7 Hz for the ions. The chemical shifts were measured with respect to TMS dissolved in 1,2-dibromo-1,1,2,2-tetrafluoroethane, which served as an external ^{19}F lock substance. The ^{13}C chemical shifts are in general agreement with literature values.

Selective irradiation of the ^1H NMR spectrum of cyclopentenone over the entire saturated region resulted in doublets of doublets for the ^{13}C NMR signals of C-1, C-2 and C-3, reflecting the reduced values of the couplings of these nuclei with H-7 and H-8. More precise sets of absolute values were subsequently obtained from a gated decoupling experiment. Definite assignments of specific ^{13}C — ^1H couplings to line separations were achieved by selective irradiation of the signals of H-7 and H-8. The ^1H NMR parameters of cyclopentenone are known and this enables the calculation of the ^{13}C sidebands in the ^1H NMR spectra

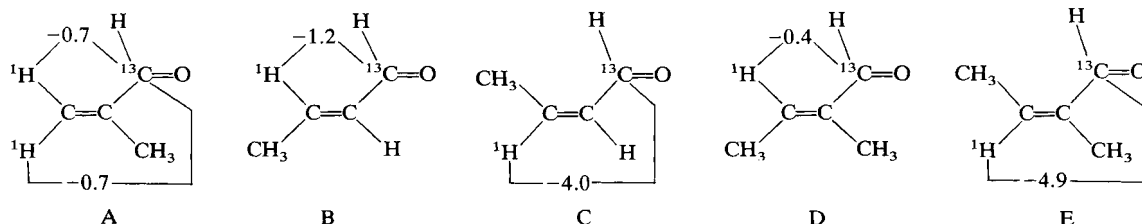
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based on the absolute values of the ^1H — ^{13}C spin couplings already obtained. The relative signs of the direct and long-range ^{13}C — ^1H couplings can now be obtained by selective irradiation of these sidebands, provided that no serious overlap of the proton lines occurs. The absolute signs have been assigned by assuming that the one bond ^{13}C — ^1H couplings are positive.

It should be realized that in the selective irradiation experiments described above the relative intensities of submultiplets, rather than single lines, have to be compared because of the couplings of C-2 and C-3 with the protons at C-4 and C-5. Because of the separation of about 0.5 ppm between the protons at C-4 and C-5 in cyclopentenone, selective decoupling of each of these is possible and was, in fact, carried out. The diagnostic value of such dual pathway couplings is, however, rather limited. Moreover, the ^1H NMR spectrum of some of the other systems was considerably more complex in the saturated region. For these reasons, no extensive study was undertaken of the interactions of the protons bonded to sp_3 carbons with the enone carbons. A similar procedure to that outlined above was followed with cyclohexenone. The C-2—H-8 and C-3—H-7 couplings were not resolved in our spectra and were thus assumed to be smaller than 0.3 Hz. The C-1—H-7 coupling was estimated to be 0.5 Hz. The signs of these interactions could not be obtained but this, however, does not affect any of the conclusions (*vide infra*). Analogous couplings were observed in protonated cyclohexenone; in protonated cyclopentenone the signs of the C-2—H-8 and C-3—H-7 couplings could not be obtained unambiguously due to the unfortunate overlap of a number of submultiplets in the ^{13}C NMR spectrum.

DISCUSSION

Cyclohex-2-ene-1-one is not a particularly strained molecule and, therefore, spin-spin couplings between ^{13}C and ^1H nuclei in acrolein and some simple, substituted derivatives can serve as suitable references for the corresponding interactions in the cyclic system. Acrolein itself has been previously studied² and recently, Vögeli and von Philipsborn published vicinal (*cis* and *trans*) three bond ^{13}C — ^1H couplings across the double bond in a large number of compounds, including some substituted acroleins as well as the corresponding carboxylic acids.³ A number of trends for $^3J(\text{CH})^c$ and $^3J(\text{CH})^t$ observed by these authors are summarized in the following scheme.

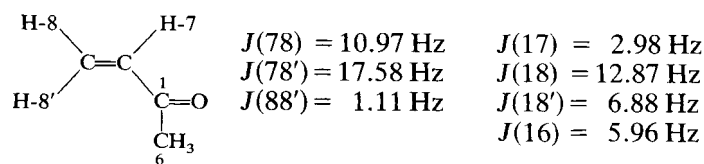


Scheme 1. Changes in three bond ^1H — ^{13}C couplings across the double bond in methyl substituted acroleins with respect to acrolein.

The large decrease in $^3J(\text{CH})^t$ observed upon introduction of a *cis*- β -methyl group (C and E) was ascribed to steric interactions between this methyl group and the formyl group, causing repolarization of the C—H bonds involved, in much the same way as implicated in the description of sterically induced chemical shifts. Similar effects were also observed for three bond couplings involving the methyl groups. It is seen in the scheme that α -methyl substitution (A) and *trans*- β -methyl substitution (B) cause only small differences in $^3J(\text{CH})^c$. The study³ also comprised acrylic acid and a number of methyl substituted derivatives. Here, only small differences were observed for $^3J(\text{CH})^c$ and $^3J(\text{CH})^t$ involving the carbonyl group, even in the case of *cis*- β -methyl substitution. The effects of α -methyl groups and *cis*- β -methyl groups upon $^3J(\text{CH})^t$ in substituted acroleins and substituted acrylic acids proved to be additive (see also Scheme 1 for acroleins).

Although the observed additivity of methyl effects upon $^3J(\text{CH})^t$ could indicate that the electronegativity of the successive methyl substituents plays an important role, Vögeli and von Philipsborn preferred to ascribe the above-mentioned small changes in $^3J(\text{CH})^c$ due to α -methyl or *trans*- β -methyl substitution to slight variations in geometry (see, however, Ref. 6).

The importance of bond angles for ^1H — ^{13}C spin-spin couplings has been stressed by Marshall and Seiwel.⁴ By analogy with ^1H — ^1H couplings, a dependence of -0.2 Hz per degree of internal angle was postulated (larger C-1, C-2, C-3 angles in acroleins should cause smaller $^3J(\text{CH})$ couplings). This trend is opposite to that observed by Vögeli and von Philipsborn for, e.g. $^3J(\text{CH})^t$ in (*Z*)-crotonic acid and acrylic acid.³ Apparently, the trends introduced by small geometric changes and/or electronic effects may be in opposite directions for $^3J(\text{CH})^t$ and $^3J(\text{CH})^c$ in acroleins and acrylic acids. Substitution at the carbonyl carbon may introduce additional changes in coupling constants involving the carbonyl carbon. This was already evident from the values in substituted acroleins and the appropriate acrylic acids.³ In the present study, evidence concerning the influence of alkyl substitution at C-1 on $^3J(\text{C-1, H-8})^t$ is provided by the results for methyl vinyl ketone as shown in Scheme 2.



Scheme 2. Coupling constants in methyl vinyl ketone.

In cyclohex-2-enone and cyclopent-2-enone the two carbonyl carbons are similarly substituted, the major difference being the change in bond angles (see Fig. 1). These bond angle differences between the 5- and the 6-membered rings are in the same direction as between sterically crowded α -substituted crotonic acids and their unsubstituted parent molecules, in this order. Yet, the *trans* coupling over three bonds is *c.* 2.7 Hz more positive in cyclopent-2-enone than in cyclohex-2-enone (Table 2). Similar experimental trends to those observed in this study have also been presented for butenedioic acids, pent-3-ene-2-ones and some derivatives including cyclic anhydrides by Braun.⁵ In his work the *trans* $^3J(\text{CH})$ couplings increase in 5-membered rings whereas the *cis* $^3J(\text{CH})$ couplings decrease, in agreement with corresponding $^3J(\text{HH})$ values.

Experimental and calculated (EHMO) values for $^3J(\text{HH})$ have been presented by Cooper and Manatt⁶ for a number of molecules, including strained, cyclic systems. Although the geometrical dependence of $^3J(\text{CH})^t$ is not entirely clear,⁴ some of the calculations in Ref. 6 would predict a smaller value of $^3J(\text{CH})^t$ in the 5-membered ring. Similar calculations based on INDO were more recently carried out on a number of substituted ethenes.⁷ Here, too, a smaller value would be

predicted for $^3J(\text{CH})^t$ in the 5-membered ring. Moreover, sizeable substitution effects on both $^3J(\text{HH})^c$ and $^3J(\text{HH})^t$ were predicted for methyl groups substituted on the double bond. No clear-cut explanations seem available at this time, except that it has been shown recently that vicinal carbon-proton and proton-proton couplings may be affected differently by certain differences in substitution and/or geometry.⁸ The four bond contribution in the 5-membered ring (dual pathway coupling) is probably small since the corresponding $^1\text{H}-^1\text{H}$ coupling is also small. Thus, there seem to be some discrepancies between our results and those of Vögeli and von Philipsborn, part of which may be caused by the fact that in the latter study the alkyl substituents attached directly to the double bond, which are absent in the present work, may cause extra changes by repolarization of the double bonds. Our semi-empirical MO calculations are in qualitative agreement with the trends as described in this paper (see next section).

Comparison of MO calculated and experimentally obtained values of $^{13}\text{C}-^1\text{H}$ spin coupling constants

In order to gain some insight into the correlation between calculated and observed $^{13}\text{C}-^1\text{H}$ couplings of the cycloalkenones and their protonated derivatives investigated in this study, we performed a number of semi-empirical MO calculations. Our main aim was to demonstrate the relationship between calculated and observed trends in coupling constants upon changing the geometries and protonating the molecule. We used the finite perturbation procedure as developed by Pople, Ostlund and McIver,⁹ coupled to CNDO/2 and INDO. Geometries obtained by MINDO/2 optimized structures were used,^{10,11} (see Fig. 1 for details).

In order to allow the separation of the effects of conjugation and the additional polarization brought about by the electronegative carbonyl oxygen in the enones, we also performed some calculations on the ethene, butadi-1,3-ene and acrolein series (see Table 1), using standard geometries. Table 1 lists the results, along with experimental couplings taken from the literature. In general, the experimental trends between ethene and butadiene are followed by both CNDO/2 and INDO, whereas the changes between the latter and acrolein are not. Several attempts were made to improve this, including, for example, a method proposed by Pople *et al.*¹² to correct for compounds with electronegative substituents. Another method was to change the Hartree-Fock matrix elements for oxygen in the CNDO/2 procedure but the improvements were only marginal. A third possibility of improving the correlation between experimental and calculated couplings is given by the adaption of Slater orbital exponents in the semi-empirical MO programs. We used the formula introduced by Grant *et al.* for the effective nuclear charge in chemical shift calculations.¹³ The effective charges were varied independently for the $2s$, $2p_{xy}$ and $2p_z$ orbitals while the CNDO/2 approximation of calculating the coulomb integrals over the valence s -orbitals was maintained. The 'best set' of Slater exponents for calculating $^2J(\text{CH})$ in ethene

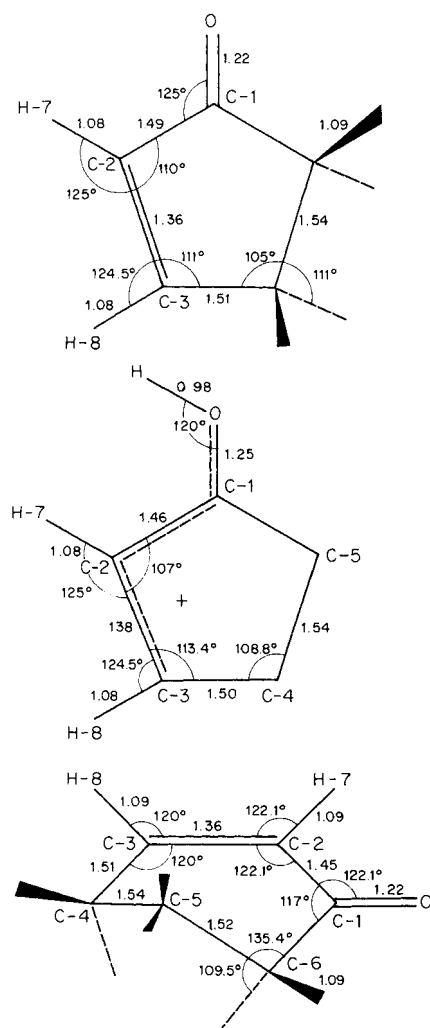


Figure 1. Molecular geometries.

Table 1. Experimental and calculated ^{13}C — ^1H spin couplings in ethene, butadi-1,3-ene and acrolein (in Hz)

	Exp ¹⁴	Ethene CNDO	INDO	Exp ¹⁵	Butadiene CNDO	INDO	Exp ²	Acrolein CNDO	INDO	^a
C-2, H-7	156.4	127.6	156.7	152.7	126.6	154.9	162.3	118.2	146.9	129.0
C-3, H-8	156.4	127.6	156.7				156.6	126.1	159.4	124.7
C-3, H-7	-2.4	-3.8	-11.6	0.01	-2.7	-10.8	0.25	-2.9	-13.6	-1.4
C-2, H-8	-2.4	-3.8	-11.6				-0.6 ¹⁶	-2.1	-12.6	-1.3
C-1, H-7				4.1	0.6	-4.2	2.2	-1.2	-9.3	0.9
C-1, H-8							15.9	10.3	20.6	7.9
H-7, H-8	11.7	8.0	9.3	10.2	7.9	9.2	10.0	8.4	10.5	5.4

^a CNDO with Slater exponentials obtained from β -values for small neutral molecules. The comparable values for ethene are: $J(\text{C-2, H-7}) = 127.1$, $J(\text{C-3, H-7}) = -2.5$, $J(\text{H-7, H-8}) = 5.4$.

proved to be in reasonable agreement with the results obtained for the shifts,¹³ but the resulting $^3J(\text{HH})$ value was rather poor. However, application of Slater's exponentials with β -values obtained from CNDO/2 calculations on ethene allows CNDO/2 to reproduce the experimental trends in the ethene, butadiene and acrolein series. The results are incorporated in Table 1. Table 2 summarizes the experimental results for cyclohex-2-enone and cyclopent-2-enone, as well as for the protonated rings. The values calculated by the CNDO/2 and INDO methods are given in Table 3. Model calculations on acrolein for different bond angles show that the more positive values of the one- and two-bond carbon-proton couplings in the 5-membered ring, in comparison with the 6-membered ring, are caused by geometric differences between the two rings.¹⁷ For the three bond couplings $^3J(\text{C-1, H-8})$ the experimental trends from acrolein to the ring systems are reproduced by CNDO for the 6-membered ring but not for the 5-membered ring. In the latter system, however, the experimental trend is reproduced by the INDO calculations. The trend from the 6- to the 5-membered ring is also reproduced by the CNDO calculations. These results are seemingly in contrast with those by Cooper and Manatt⁶ for proton-proton coupling constants in strained olefins.

Table 2. Experimental spin couplings of the enone moieties of cyclopent-2-enone and cyclohex-2-enone, and their protonated derivatives

	^a	^b	^c	^d
C-2, H-7	170.4	162.3	180.7	174.0
C-3, H-7	4.4	0.3	2.5	0.4
C-2, H-8	4.5	0.3	2.4	0.4
C-3, H-8	166.2	157.5	173.7	164.8
C-1, H-7	5.65	0.5	4.2	0.4
C-1, H-8	12.97	10.3	12.85	11.1
H-7, H-8	5.74	10.5	5.2	

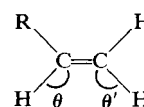
^a Cyclopent-2-enone.

^c Protonated cyclopent-2-enone.

^b Cyclohex-2-enone.

^d Protonated cyclohex-2-enone.

By EHMO calculations they predicted that *cis* and *trans* olefinic couplings become larger as θ and/or θ' in the fragment



are diminished.

Their calculations reproduced the experimental trends for the *cis* coupling in a number of compounds but the situation for the *trans* coupling, with which we are concerned here, is less clear,⁴ especially because in this case the calculated results were not compared with the experimental.

The trends observed after protonation of the 5-membered ring are not borne out by the calculations. This cannot be accounted for entirely by geometric changes brought about by the protonation, which can be concluded from INDO calculations on acrolein as well as on the protonated form for different geometries.¹⁷ Subsequently, the couplings in cyclopent-2-enone and the protonated derivative were calculated using effective nuclear charges with molecular screening parameters derived from β -values for small neutral molecules,¹³ by extrapolation to the bond distances calculated previously for both systems (see above). The results reproduce the differences within a given skeleton better than with the uncorrected MO program (see Table 3). We finally tried to approach the screening term β via overlap populations by means of the equation $Z^* = \beta Z^{(0)} - sq$ in which $q = \sum_{\mu} P_{\mu\mu}^A$ and $\beta = \sum_{B \neq A} P_{\mu\nu} S_{\mu\nu} - 1.38$. The $2s$ and $2p$ orbitals have been given equal orbital exponentials in these calculations. Although the absolute values of some couplings calculated in this way are still relatively different from the experimental values, these calculations predict a better trend for the C-3, H-7 coupling when compared with CNDO/2 with Slater exponentials. A better differentiation between one bond and long-range couplings is also achieved in this way.

Table 3. Calculated coupling constants of the enone parts of cyclopent-2-enone and cyclohex-2-enone as well as for the protonated derivatives

	a	b	c	d	e	f	g	h
C-2, H-7	110.2	120.8	146.2	128.2	181.1	157.9	208.7	158.2
C-3, H-7	-1.86	0.76	-6.82	0.80	4.29	1.23	4.17	-4.05
C-2, H-8	-0.56	0.37	-8.40	0.87	2.66	2.67	5.48	-1.67
C-3, H-8	122.5	124.5	152.5	125.3	171.4	126.1	155.9	155.1
C-1, H-7	0.35	3.18	-1.68	3.33	8.25	3.05	5.99	0.79
C-1, H-8	8.36	11.11	18.76	8.27	12.00	10.65	13.63	18.02
H-7, H-8	8.51	3.80	4.84	3.11	1.85	2.56	1.55	3.1

^a Cyclohex-2-enone, CNDO/2.

^b Cyclopent-2-enone, CNDO/2.

^c Cyclopent-2-enone, INDO.

^d Cyclopent-2-enone, CNDO/2 with Slater exponentials obtained from small, neutral molecules (see text).

^e Cyclopent-2-enone, CNDO/2 with β values via over-

lap populations (see text).

^f Protonated cyclopent-2-enone, CNDO/2 with Slater exponentials obtained from small, neutral molecules (see text).

^g Protonated cyclopent-2-enone, CNDO/2 with β values via overlap populations (see text).

^h Protonated cyclopent-2-enone, INDO.

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