

## References and Notes

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## Application of $^{13}\text{C}$ Nuclear Magnetic Resonance Spectroscopy to the Analysis of Charge Distribution Patterns in Unsaturated Carbonyl-Containing Compounds<sup>1</sup>

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**Abstract:** The proton decoupled carbon-13 nuclear magnetic resonance spectra of a variety of unsaturated carbonyl-containing compounds, as well as the corresponding alkenes, saturated carbonyl derivatives, and alkanes, have been recorded. An empirical treatment is described which relates the obtained data to the relative  $\pi$  charge densities at the various molecular centers. The relative densities are shown to be consistent with expectations.

Carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectroscopy has found wide and increasing application to problems of chemical interest. One area in which  $^{13}\text{C}$  NMR spectroscopy has served as a sensitive probe is the analysis of charge distributions in organic ions.<sup>2</sup> The increased advantage of carbon over proton magnetic resonance in such systems stems from its increased sensitivity to substituent effects. This is due to the fact that the carbon nucleus is directly bonded to the substituents which donate or withdraw electrons. The proton, on the other hand, monitors the same situation, but from a position once further removed. The approximately 20-fold greater chemical shift range of carbon-13 nuclei as compared to protons also allows for easier identification of the factors responsible for chemical shift differences.

These same features should serve to benefit the investigation of charge distributions in neutral molecules as well. Indeed, a number of generalizations along these lines have been made.<sup>3</sup> Still, the application of  $^{13}\text{C}$  NMR spectroscopy to the study of charge variations in neutral, nonaromatic molecules has been much more limited than the role it plays in the corresponding analysis of ions.

Some correlation should exist between  $^{13}\text{C}$  NMR chemical shifts and charge densities. It is the paramagnetic screening constant ( $\sigma_p$ ) which is thought to control the  $^{13}\text{C}$  chemical shift in most cases.<sup>4</sup> The sophisticated expressions developed by Ditchfield and others,<sup>5</sup> as well as the earlier equations of Pople and Karplus,<sup>6</sup> all contain terms which relate  $\sigma_p$  to local atomic charge densities. However, these same expressions also reveal dependencies upon bond orders, orbital energy differences, and

other parameters which are not directly related to the sought after atomic densities. Hence, while a relationship between charge densities and  $^{13}\text{C}$  NMR shifts is to be expected, it need not be linear.

Some time ago, we elected to carry out a detailed analysis of the  $^{13}\text{C}$  NMR spectra of a wide variety of unsaturated carbonyl containing systems. The establishment of a correlation between  $\pi$  charge densities and empirically modified chemical shifts within this series of compounds would be quite significant. Not only would it bode well for extension to other classes of compounds, but it would have a number of immediate applications. It would provide a simple method for obtaining a clear electronic description of a molecule. This technique, unlike theoretical calculations, would not involve assumptions concerning molecular geometry or solvation; observations would be made directly on the molecules in solution. Such a method would also allow us to comment upon the aromatic character of appropriate systems, annulenones, for example. Furthermore, as molecular orbital coefficients and PMO theory serve to relate charge densities to reaction rates,<sup>7</sup> we would hope to eventually apply any such correlation and methodology to the prediction of chemical reactivity.

Our initial efforts with  $\alpha,\beta$ -unsaturated carbonyl compounds were centered on evaluating the relationship between the  $\beta$ -carbon atom  $^{13}\text{C}$  NMR shift and the corresponding  $\pi$ -electron density. Our approach is wholly empirical and proceeds as follows. We ascribe the shift difference between the  $\beta$ -carbon atom in the enone and the analogous carbon atom in the corresponding alkene to the total ( $\sigma + \pi$ ) electron deficiency at

Table I.  $^{13}\text{C}$  NMR Shifts<sup>a</sup>

|  |  |                                      |                                      |  |  |                                  |                          |
|--|--|--------------------------------------|--------------------------------------|--|--|----------------------------------|--------------------------|
| <br>137.5<br>128.8                     | <br>140.7<br>113.2                     | <br>36.9<br>7.9                      | <br>25.1<br>13.8                     | <br>130.0<br>150.5   | <br>127.3  | <br>42.0<br>27.1                 | <br>27.0                 |
| <br>136.5                              | <br>124.5                              | <br>36.7                             | <br>27.0                             | <br>134.6<br>164.9   | <br>130.7  | <br>38.2<br>23.2                 | <br>25.9                 |
| <br>81.9<br>78.1                       | <br>86.0<br>67.4                       | <br>36.9<br>7.9                      | <br>25.1<br>13.8                     | <br>136.2<br>141.4   | <br>130.4, 128.4 <sup>b</sup>                                      | <br>42.0<br>25.7                 | <br>26.8                 |
| <br>133.0<br>143.5                     | <br>133.2<br>123.6                     | <br>45.7<br>17.4                     | <br>34.2<br>22.4                     | <br>128.7 <sup>c</sup><br>138.4 <sup>d</sup><br>131.5 <sup>e</sup><br>136.9 <sup>d</sup> | <br>131.3, 126.0 <sup>e</sup>                                      | <br>42.0<br>25.7<br>27.3<br>24.8 | <br>26.8                 |
| <br>124.3<br>155.0                     | <br>126.7<br>130.7                     | <br>52.8<br>24.6                     | <br>41.5<br>27.8                     | <br>21.2<br>10.7   | <br>12.9<br>4.3  | <br>41.7<br>18.2                 | <br>29.8<br>22.3         |
| <br>145.0<br>125.5                     | <br>147.8<br>108.4                     | <br>41.7<br>18.2                     | <br>29.8<br>22.3                     | <br>20.7<br>10.6   | <br>10.6<br>4.1  | <br>38.9<br>18.6                 | <br>25.6<br>22.9         |
| <br>106.7<br>163.2<br>OCH <sub>3</sub> | <br>105.0<br>146.7<br>OCH <sub>3</sub> | <br>43.7<br>67.6<br>OCH <sub>3</sub> | <br>31.8<br>72.7<br>OCH <sub>3</sub> | <br>137.2<br>128.6<br>128.3  | <br>144.4<br>128.4 <sup>b</sup><br>128.0 <sup>b</sup>              | <br>51.5<br>28.5<br>25.7         | <br>39.6<br>33.2<br>26.7 |
| <br>118.3<br>155.6                     | <br>101.1<br>141.1                     | <br>42.9<br>67.8                     | <br>26.7<br>68.7                     | <br>160.8  | <br>109.6  | <br>30.8 <sup>20</sup>           | <br>18.6                 |
| <br>138.6<br>137.7                     | <br>133.7<br>115.6                     | <br>37.3<br>6.0                      | <br>16.5<br>16.3                     | <br>137.2<br>128.6<br>128.3  | <br>144.4<br>128.4 <sup>b</sup><br>128.0 <sup>b</sup>              | <br>51.5<br>28.5<br>25.7         | <br>39.6<br>33.2<br>26.7 |
| <br>128.2<br>133.1                     | <br>137.5<br>115.1                     | <br>27.5<br>8.9                      | <br>25.9<br>10.2                     | <br>137.2<br>128.6<br>128.3  | <br>144.4<br>128.4 <sup>b</sup><br>128.0 <sup>b</sup>              | <br>51.5<br>28.5<br>25.7         | <br>39.6<br>33.2<br>26.7 |
| <br>130.4<br>127.6                     | <br>140.0<br>113.6                     | <br>29.0<br>9.7                      | <br>27.1<br>11.4                     | <br>142.1 <sup>c</sup><br>136.1 <sup>c</sup><br>134.7 <sup>c</sup>                       | <br>120.8 <sup>c</sup><br>126.7 <sup>c</sup><br>131.0 <sup>c</sup> | <br>43.9<br>24.4<br>30.5         | <br>28.5                 |
| <br>132.5<br>141.5                     | <br>130.2                              | <br>42.0<br>25.7                     | <br>26.8                             | <br>143.0  | <br>135.4  | <br>27.3                         | <br>29.8                 |
| <br>132.5<br>146.3                     | <br>132.5                              | <br>43.9<br>24.4                     | <br>26.5                             |  |  |                                  |                          |

<sup>a</sup> All chemical shifts are reported in parts per million downfield from internal Me<sub>4</sub>Si. <sup>b</sup> Signals unassigned, average value used in computations. <sup>c, d</sup> Signals unassigned; interchange has no effect on computations. <sup>e</sup> Reference 2a, p 77. <sup>f</sup> N. Werstiuk, R. Taillefer, R. A. Bell, and B. Sayer, *Can. J. Chem.*, **51**, 3010 (1973).

the enone  $\beta$ -carbon atom. In order to convert this shift differential into the fraction of an electron gained or removed, we divide by 240 ppm/electron. This value has been selected as it lies close to recent estimates for both  $\pi$  and  $\sigma$  systems. For example, it resides within the experimental extremes of 100–300 ppm/ $\pi$  electron determined by other investigators<sup>8</sup> and is close to Hehre's appraisal of 246 ppm/ $\pi$  electron for electron-deficient ions.<sup>9</sup> We use this factor as well for  $\sigma$  electrons since Fliszár et al.<sup>10</sup> have inferred a value of 237.1 ppm/ $\sigma$  electron. We note that any error introduced by this parameter will certainly affect the absolute accuracy of the ultimately determined  $\pi$  densities. However, since these same approximations are necessarily applied to every molecular series studied, it was our hope that the *relative*  $\pi$  densities obtained would still be informative.

Using methyl vinyl ketone as an example, we find that the total electron deficiency at the  $\beta$ -carbon atom is given by eq 1

$$Z_{\beta}^t = (128.8 - 113.2)/240 = 0.065 \text{ electrons} \quad (1)$$

to be 0.065 electron. The symbol  $Z_n^t$  is used to denote the charge density at the  $n$ th carbon atom and the superscript  $\pi$ ,  $\sigma$ , or  $t$  indicates that it is the  $\pi$ ,  $\sigma$ , or total electron density which is being calculated at this atom. The chemical shifts employed in eq 1 are taken from Table I. According to eq 2,

$$Z_n^t = Z_n^{\pi} + Z_n^{\sigma} \quad (2)$$

the total electron density may be viewed as a composite of the  $\sigma$  and  $\pi$  components at any given center. Since we are primarily interested in the  $\pi$  distribution, we must find a method to solve for  $Z_n^{\sigma}$  and then subtract it from the previously obtained  $Z_n^t$  value. Our approach here involves the assumption that the  $\sigma$  effect of the carbonyl group on the  $\beta$ -carbon atom in methyl vinyl ketone can be equated to the  $\sigma$  effect of the carbonyl on

Table II

| Compound                              | $Z_{\alpha}^{\pi}$              | $Z_{\beta}^{\pi}$                                   |
|---------------------------------------|---------------------------------|---|
| Cyclopentadienone                     |                                 | -0.111 ( $Z_{\Sigma}^{\pi}$ )                       |
| <i>p</i> -Benzoquinone                |                                 | 0.107 ( $Z_{\Sigma}^{\pi}$ )                        |
| Norborn-5-en-2-one                    |                                 | 0.042 ( $Z_{\gamma}^{\pi}$ )                        |
| Cyclooct-2-enone                      | -0.053                          | 0.051   |
| Acrylamide                            | -0.048                          | 0.066   |
| But-3-yn-2-one                        | -0.066                          | 0.069   |
| Cyclohept-2-enone                     | -0.064                          | 0.074   |
| Acrylic acid                          | -0.046                          | 0.080   |
| Cyclopropyl methyl ketone             | -0.015                          | 0.087 ( $Z_{\beta,\beta'}^{\pi}$ )                  |
| Cycloocta-2,4-dienone                 | -0.053                          | 0.087 ( $Z_{\beta,\delta}^{\pi}$ )                  |
| 3-Methylbut-3-en-2-one                | -0.061                          | 0.088   |
| <i>trans</i> -4-Methoxybut-3-en-2-one | -0.042                          | 0.090   |
| Methyl vinyl ketone                   | -0.062                          | 0.090   |
| Acetophenone                          | -0.071 ( $Z_{\alpha,m}^{\pi}$ ) | 0.091 ( $Z_{o,p}^{\pi}$ )                           |
| Cyclohex-2-enone                      | -0.051                          | 0.097   |
| <i>trans</i> -Pent-3-en-2-one         | -0.049                          | 0.104   |
| Cycloocta-2,7-dienone                 | -0.071                          | 0.109 ( $Z_{\beta,\beta'}^{\pi}$ )                  |
| 4-Methylpent-3-en-2-one               | -0.057                          | 0.114   |
| $\gamma$ -Pyrone                      | 0.008                           | 0.129 ( $Z_{\beta,\beta'}^{\pi}$ )                  |
| Acrolein                              | -0.066                          | 0.135   |
| Cyclopent-2-enone                     | -0.035                          | 0.154   |
| Tropone                               |                                 | 0.175 ( $Z_{\Sigma}^{\pi}$ )                        |
| Dicyclopropyl ketone                  | -0.026                          | 0.181 ( $Z_{\beta,\beta',\beta'',\beta'''}^{\pi}$ ) |
| Di- <i>n</i> -propylcyclopropenone    |                                 | 0.393 ( $Z_{\Sigma}^{\pi}$ )                        |

the  $\beta$ -carbon atom in methyl ethyl ketone. Clearly, this is an approximation as the former  $\sigma$  skeleton involves  $sp^2$ - $sp^2$  bonding, while it is more nearly  $sp^3$ - $sp^3$  in the latter system. Again, any errors introduced by this approximation would, hopefully, not invalidate the relative trends observed. This formalism does allow us to obtain  $Z_n^{\sigma}$ , and consequently  $Z_n^{\pi}$ , by measuring the chemical shifts of the corresponding carbon atoms in the saturated analogues of the alkenone and alkene under investigation. Continuing with methyl vinyl ketone as an example, we now require the  $^{13}\text{C}$  NMR shifts of C(4) in methyl ethyl ketone and C(1) in butane. Subtraction of these two values followed by division of the resultant  $\sigma$  shift differential by 240 ppm/electron yields  $Z_{\beta}^{\sigma}$ . Subtracting this term from  $Z_{\beta}^t$  yields  $Z_{\beta}^{\pi}$  as shown below

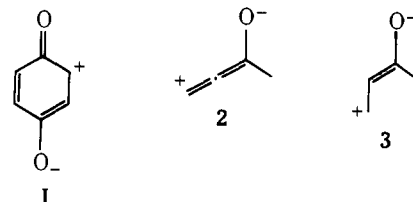
$$Z_{\beta}^{\pi} = Z_{\beta}^t - Z_{\beta}^{\sigma} = [(128.8 - 113.2) - (7.9 - 13.8)]/240 = 0.090 \text{ electron} \quad (2a)$$

If correct, this analysis indicates that 9% of a  $\pi$  electron has been removed from the  $\beta$ -carbon atom in methyl vinyl ketone. While the absolute accuracy of this estimate remains to be further verified, we note that it does fall near the range of values generated via theoretical calculations.<sup>11</sup>

Hence, as illustrated above, for each enone to be examined, we need three additional compounds in order to complete the analysis. Along with the alkenone, the corresponding alkene, alkanone, and alkane are required. The requisite  $^{13}\text{C}$  NMR data and the resultant  $Z_{\beta}^{\pi}$  indexes are presented in Tables I and II, respectively.<sup>12</sup> The following is a discussion of these results.

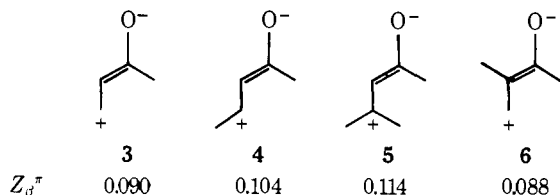
### Results and Discussion

Analysis of *p*-benzoquinone yields  $Z_{\Sigma}^{\pi} = 0.039$  electron. The subscript  $\Sigma$  denotes a summation of the electron density over all of the olefinic carbon atoms, in the case at hand, the four equivalent  $\beta(\alpha)$ -carbon atoms. On a per carbon basis  $Z_{\beta}^{\pi} = 0.010$  for this molecule. Assuming methyl vinyl ketone to be a relatively normal enone, the low value obtained for *p*-benzoquinone requires comment. It is well known that a cationic center adjacent to a carbonyl is strongly destabilized. Just such a situation is depicted in **1**, the 1,4-dipolar resonance hybrid in which  $\pi$ -electron density has been removed from the  $\beta$ -carbon atom in *p*-benzoquinone. Destabilization of this type

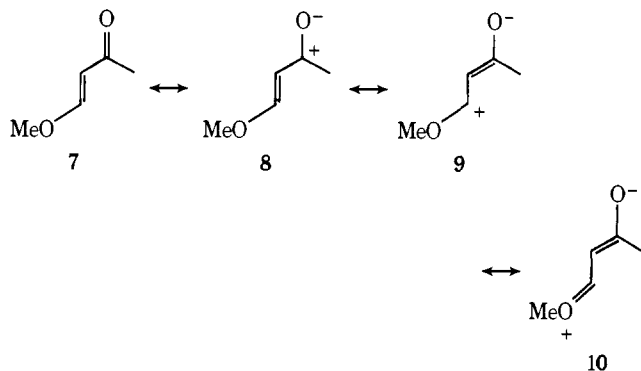


of contributor presumably accounts for the decreased  $Z_{\Sigma}^{\pi}$  value observed. An equivalent view notes that the olefinic carbon atoms in *p*-benzoquinone are simultaneously located  $\alpha$  to one carbonyl and  $\beta$  to the other. Therefore, their  $Z^{\pi}$  indexes should reflect an average of these two environments. For the reason described above, typical  $Z_{\alpha}^{\pi}$  values are expected to be much smaller than the corresponding  $Z_{\beta}^{\pi}$  indexes. In fact,  $Z_{\alpha}^{\pi}$  is generally of the opposite sign as  $Z_{\beta}^{\pi}$  (vide infra). Hence, a reduced  $Z^{\pi}$  index is anticipated and observed for *p*-benzoquinone. In but-3-yn-2-one,  $Z_{\beta}^{\pi} = 0.069$ , still significantly reduced from the value in its vinylic analogue, methyl vinyl ketone. Here the explanation hinges on the stability difference between propargylic and allylic cations. Propargylic halides are known to solvolyze several orders of magnitude slower than their allylic counterparts. This has been attributed to an inductive destabilization rather than an instability of the allenic resonance contributor.<sup>13,14</sup> It has also been demonstrated both experimentally<sup>15a</sup> and theoretically<sup>15b</sup> that propargyl cations are less delocalized than their allylic counterparts. Hence,  $Z_{\beta}^{\pi}$  is smaller in the acetylenic system, as compared to its vinylic analogue, not because allenyl structures such as **2** are less stable than allylic hybrids such as **3**, but rather because there is simply less charge separation to begin with in the propargylic carbonyl and less of the charge is delocalized to the  $\beta$  position.

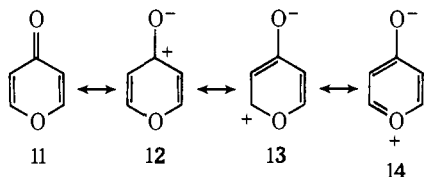
Comparison of  $Z_{\beta}^{\pi}$  for methyl vinyl ketone with the corresponding indexes from a series of methylated derivatives is of interest. The data reveal that, as anticipated,  $\beta$  substitution by a stabilizing methyl group results in an increased  $Z_{\beta}^{\pi}$  value, while  $\alpha$  substitution, which locates the substituent at a position where interaction is minimal, results in essentially the same  $Z_{\beta}^{\pi}$  value as observed in the parent compound. We have also replaced the  $\beta$  methyl group with a methoxy appendage (*trans*-4-methoxybut-3-en-2-one). The increased stability of methoxylated cations can be attributed to the possibility of



increased delocalization as depicted by canonical form **10**. To the extent that such stabilizing interactions are involved in neutral molecules, a decrease in  $Z_{\beta^{\pi}}$  should result. The  $Z_{\beta^{\pi}}$  index for this methoxybutenone was found to be 0.090, smaller than that in the corresponding pentenone. If some method could be devised to further enhance the significance of contributors such as **10**, a further decrease in the  $Z_{\beta^{\pi}}$  index should



result. Such an effect was observed with  $\gamma$ -pyrone. The basic valence bond structures are now given by hybrids such as **11**–**14**. The importance of **14**, the analogue of **10**, should be



increased due to the inherent stability of the aromatic pyrylium system. The  $Z_{\beta,\beta^{\pi}}$  index determined for  $\gamma$ -pyrone was 0.129. Hence, on a per carbon atom basis,  $Z_{\beta^{\pi}}$  in  $\gamma$ -pyrone is only 0.064, reduced considerably below the value obtained for *trans*-4-methoxybut-3-en-2-one. This seems explicable within the framework of the above argument. Increased participation by structures such as **14** has resulted in a decreased contribution from other hybrids such as **13** with a concomitant increase in  $\pi$ -electron density at the  $\beta$ -carbon atom.

Comparison of acrolein ( $Z_{\beta^{\pi}} = 0.135$ ), methyl vinyl ketone ( $Z_{\beta^{\pi}} = 0.090$ ), acrylic acid ( $Z_{\beta^{\pi}} = 0.080$ ), and acrylamide ( $Z_{\beta^{\pi}} = 0.066$ ) is also instructive. In this series, it is only the substituent attached directly to the carbonyl carbon which is being varied. As this appendage becomes better able to stabilize a positive charge inductively and/or through resonance, less charge is dispersed to the  $\beta$ -carbon with a consequent decrease in  $Z_{\beta^{\pi}}$  as observed.

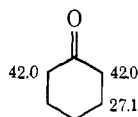
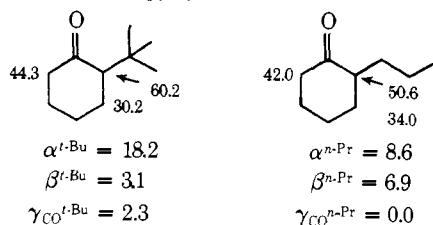
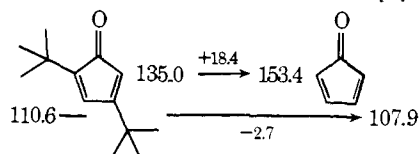
The cycloalkenones form another interesting series. Progression from cyclooct-2-enone ( $Z_{\beta^{\pi}} = 0.051$ ) to cyclohept-2-enone ( $Z_{\beta^{\pi}} = 0.074$ ) to cyclohex-2-enone ( $Z_{\beta^{\pi}} = 0.097$ ) to cyclopent-2-enone ( $Z_{\beta^{\pi}} = 0.154$ ) results in a steady decrease in  $\pi$ -electron density at the  $\beta$ -carbon atom. The series limits would be imposed by cyclopropenone ( $Z_{\beta^{\pi}} = 0.197$ /carbon atom; *vide infra*) at one extreme and a very large ring alkenone, approximated by *trans*-pent-3-en-1-one ( $Z_{\beta^{\pi}} = 0.104$ ), at the other. We feel that there are two effects contributing to the decrease in  $Z_{\beta^{\pi}}$  from both ends of the series. Cyclohexenone and cyclopentenone are planar or nearly so. The molecular frameworks position the p-orbitals in a continuous parallel array, permitting strong resonance interaction between the

carbonyl and olefinic moieties. As the number of methylene links connecting  $C_{\beta}$  to the carbonyl is decreased, the molecule approaches the cyclopropenone configuration. This has two important consequences; first, as the  $C_{\beta}$ -CO internuclear separation decreases, more charge can be separated for the same amount of work. Secondly, the molecule should begin to enjoy the same stabilizing effects bestowed upon cyclopropenone by polarization. Both of these changes should result in increasing  $Z_{\beta^{\pi}}$  indexes as one tends to smaller rings. Olah and Liang have noticed a parallel trend in regards to the stability of the corresponding allylic cycloalkenyl cations.<sup>16</sup> For cycloalkenones larger than cyclohexenone, continued increase in the length of the methylene chain through the medium ring sizes does not bring about any marked change in the  $C_{\beta}$ -CO internuclear separation, but rather, causes a twisting about the carbon-carbon single bond connecting the carbonyl and the olefinic groups. This reduces the resonance coupling of these two units with a resultant decrease in  $Z_{\beta^{\pi}}$ . When the methylene chain becomes so large that the ring can be approximated by an acyclic system, a planar *s-cis* or *s-trans* conformation once again becomes possible, and  $Z_{\beta^{\pi}}$  should rise from the medium ring low point to a value close to that found in the open-chain systems discussed above. A similar twisting argument has been advanced by Heap et al. in order to explain the changing chemical shift differences between  $H_{\alpha}$  and  $H_{\beta}$  in a series of medium ring enones.<sup>17</sup>

We have also investigated a number of dienones, and the results are typified by those found in the cyclooctyl series. As mentioned above, cyclooct-2-enone was found to have  $Z_{\beta^{\pi}} = 0.051$ . Cycloocta-2,7-dienone, a cross-conjugated system, has  $Z_{\beta,\beta^{\pi}} = 0.109$ . Again, this value is the sum from the two equivalent  $\beta$  positions and is essentially twice the value obtained from the monoene. This indicates that, at least formally, the cross-conjugated dienone may be viewed as being composed of two separate noninteracting enone units. Cycloocta-2,4-dienone was also examined.  $Z_{\beta,\beta^{\pi}}$  for this molecule represents the summation over the  $\beta$ - and  $\delta$ -carbon atoms and is equal to 0.087, a value larger than that found for cyclooctenone, but smaller than that for cycloocta-2,7-dienone. This is in accord with the general observation that  $\pi$  energies and other properties dependent upon conjugation begin to level off with increasing extension of unsaturation.<sup>18</sup>

As stated at the outset, we had hopes of applying this methodology to the analysis of aromatic character in the appropriate systems. In this regard we have studied the first three members of the annulenone family. The first member of this series is cyclopropenone. However, for reasons based on both accessibility and stability, we have selected the 1,2-di-*n*-propyl derivative for study. Therefore, 1,2-di-*n*-propylcyclopropene, 1,2-di-*n*-propylcyclopropane, and 2,3-di-*n*-propylcyclopropanone were required for complete analysis. Since this last compound was expected to be relatively unstable,<sup>19</sup> we substituted the available <sup>13</sup>C NMR data from Greene's *trans*-1,2-di-*tert*-butylcyclopropanone.<sup>20</sup> We have attempted to correct for the differing effects of a *tert*-butyl vs. an *n*-propyl substituent through an analysis of the <sup>13</sup>C NMR shifts observed for cyclohexanone,  $\alpha$ -*tert*-butylcyclohexanone, and  $\alpha$ -*n*-propylcyclohexanone. These three molecules, along with the relevant chemical shifts, are displayed in Chart I. These data allow us to calculate typical  $\alpha$  and  $\beta$  substituent parameters for these two appendages as well as  $\gamma_{CO}$  corrections, which represent the substituent effect on the  $\gamma$ -carbon atom across the carbonyl carbon. Equation 3 utilizes these param-

$$\begin{aligned} \delta_{C_2^{n-Pr}} &= \delta_{C_2^{t-Bu}} - (\alpha^{t-Bu} + \beta^{t-Bu} + \gamma_{CO}^{t-Bu}) \\ &\quad + (\alpha^{n-Pr} + \beta^{n-Pr} + \gamma_{CO}^{n-Pr}) \\ &= 30.8 - (18.2 + 3.1 + 2.3) + (8.6 + 6.9 + 0.0) \\ &= 22.7 \text{ ppm} \end{aligned} \quad (3)$$

**Chart I.**  $^{13}\text{C}$  NMR Shifts for  $\alpha$ -*tert*-Butyl<sup>12</sup> and  $\alpha$ -*n*-Propylcyclohexanone**Chart II.** Estimation of the  $^{13}\text{C}$  NMR Shifts in [5]Annulenone

eters in order to estimate the  $^{13}\text{C}$  NMR shift for C(2) ( $\delta_{\text{C}2}$ ) in *trans*-2,3-di-*n*-propylcyclopropanone. Combining this chemical shift with those of the appropriate analogues contained in Table I, in the fashion described above, yields  $Z_{\Sigma}^{\pi} = 0.393$ . Even on a per carbon atom basis, this is the largest  $Z^{\pi}$  value we have observed. It clearly reflects the dramatic polarization within this molecule ( $\mu_{\text{exp}} = 4.78 \text{ D}^{22}$ ). Furthermore, Schweig et al.,<sup>23</sup> on the basis of photoelectron data and CNDO calculations, estimate that 0.33  $\pi$  electron has been removed from the olefinic unit in di-*tert*-butylcyclopropenone.

Continuing with [5]annulenone, we have focused upon the 2,4-di-*tert*-butyl derivative for reasons of stability; the requisite chemical shifts from cyclopentadiene, cyclopentanone, and cyclopentene were used to complete the analysis. Of course, the  $^{13}\text{C}$  NMR shifts for 2,4-di-*tert*-butylcyclopentadienone could not be compared directly with those of the three unsubstituted compounds, but rather again, the effects of the *tert*-butyl groups needed to be taken explicitly into account. This was accomplished by comparing the  $^{13}\text{C}$  NMR shifts in 3,5-di-*tert*-butyl-*o*-quinone<sup>24</sup> to those in the parent quinone.<sup>24</sup> This permitted us to estimate the necessary *tert*-butyl correction factors as detailed in Table III. Using these values to modify the di-*tert*-butylcyclopentadienone chemical shifts contained in Table I, we were able to estimate the  $^{13}\text{C}$  NMR shifts expected for [5]annulenone itself. The results are displayed in Chart II. Combination of these estimated shifts in the standard fashion with the shifts observed for the other five-membered ring derivatives yields  $Z_{\Sigma}^{\pi} = -0.111$ . This is the only system which we have studied that produces a negative index. Such a value is understandable in terms of a change in polarization in cyclopentadienone. Charge displacement as in more typical ketones would give weight to hybrids such as **15**. Such structures, akin to the cyclopentadienyl cation, should be markedly destabilized. On the other hand, should the polarization tend to be as depicted in **16**, in accord with the



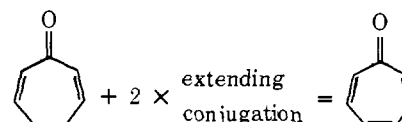
negative  $Z_{\Sigma}^{\pi}$  value, a seemingly more stabilized system related to the aromatic cyclopentadienyl anion could develop. Again on the basis of photoelectron spectral data, Schweig et al.<sup>23</sup> have concluded that the olefinic carbon atoms in cyclopenta-

**Table III.** *tert*-Butyl Correction Factors for [5]Annulenone

|      | 3,5-Di- <i>tert</i> -butyl- <i>o</i> -quinone <sup>24</sup> | <i>o</i> -Quinone <sup>24</sup> | Annulenone correction factor |
|------|---|---------------------------------|------------------------------|
| C(4) | 133.1   | 130.4                           | -2.7                         |
| C(6) | 121.6   | 140.0                           | +18.4                        |

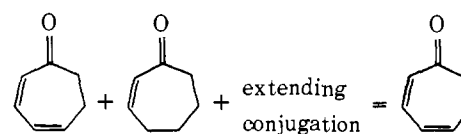
dienone bear considerably more  $\pi$  electron density than analogous carbons in more typical systems. Garbisch had previously arrived at the same conclusion through an analysis of the proton magnetic resonance spectrum of several cyclopentadienones.<sup>25</sup> Schweig has also reported CNDO calculations on the parent system which indicate that no  $\pi$  electron density is transferred from the dienyl unit to the carbonyl.<sup>23</sup> The magnitude of our result is somewhat (ca. 11%) larger than that from the CNDO calculation. However, it should be realized that our result is for the molecule in solution; this effect should tend to increase the polarization above that estimated via computer calculation. Clearly, the direction of our result is in accord with experiment.

So far then, we see a dramatic alternation as we proceed from [3]- to [5]annulenone, in line with current ideas on aromaticity. [7]Annulenone or tropone is the highest member of this series which we have investigated. Recent claims based on both theory<sup>26</sup> and experiment<sup>27</sup> suggest that this molecule would be best classified as a polyunsaturated ketone with enhanced  $\pi$  polarization. The molecule is certainly not as aromatic or polarized as cyclopropenone, nor, on the other hand, is the aromaticity completely damped out. On the basis of compounds already evaluated, we can estimate a  $Z_{\Sigma}^{\pi}$  index for a nonaromatic tropone molecule. Using the  $Z^{\pi}$  difference between cyclooct-2-enone and cycloocta-2,4-dienone ( $\Delta Z^{\pi} = 0.036$ ) as a measure of the increase in  $Z^{\pi}$  occurring upon extension of conjugation, we can proceed as follows. Taking twice this value, because we are formally extending each enone branch, and adding it to  $Z_{\alpha,\alpha',\beta,\beta'}^{\pi} = 0.009$  from cyclohepta-



$$Z^{\pi} = 0.009 + 2(0.036) = 0.08$$

2,6-dienone<sup>28</sup> yields  $Z_{\Sigma}^{\pi} = 0.08$ . Alternately, the problem can be approached from cyclohepta-2,4-dienone<sup>29</sup> as illustrated below. Again, a  $Z_{\Sigma}^{\pi}$  value in the vicinity of 0.08 is predicted.



$$Z^{\pi} = 0.034 + 0.010 + (0.036) = 0.08$$

If tropone were really an aromatic structure with **17** making a strong contribution, an index in excess of 0.08 would be anticipated. From the data in Table I we find  $Z_{\Sigma}^{\pi} = 0.176$ , in accord with the above referenced theoretical and experimental results, which classify this molecule as a borderline entity. Additionally, our estimate is again in excellent agreement with

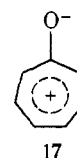
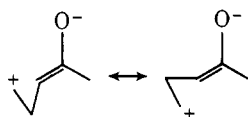


Table IV. Calculated  $\pi$  Densities for *s-trans*-Acrolein

| Method          | $Z_{\beta}^{\pi}$ (calcd) | Ref |
|-----------------|---------------------------|-----|
| MINDO/2         | 0.035                     | 11a |
| CNDO/2          | 0.047                     | 11b |
| CNDO/2          | 0.051                     | 11a |
| CNDO/S          | 0.055                     | 11a |
| INDO            | 0.060                     | 11a |
| STO-4-31G       | 0.080                     | 31  |
| Extended Hückel | 0.115                     | 11a |
| Hückel          | 0.228                     | 11a |

Schweig's measure (0.18  $\pi$  electron)<sup>23</sup> of the  $\pi$  electron deficiency in the trienyl segment of this compound.

Our methodology is not limited to olefinic compounds. Much evidence has accumulated in the literature which suggests that certain similarities exist between carbon-carbon double bonds and cyclopropyl groups. We have therefore investigated cyclopropyl methyl ketone and dicyclopropyl ketone. As discussed earlier, we require four compounds in order to complete our analysis: the alkenone, alkene, alkanone, and alkane. In the cyclopropyl series, these correspond to the cyclopropyl ketone, cyclopropyl alkane, isopropyl ketone, and isopropyl alkane, respectively.  $Z_{\beta,\beta'}^{\pi}$  for cyclopropyl methyl ketone was found to be 0.087. In dicyclopropyl ketone,  $Z_{\beta,\beta',\beta'',\beta'''}^{\pi} = 0.181$ , again mirroring the doubling pattern observed in the di- $\alpha,\beta$ -unsaturated ketone family.



Analysis of acetophenone yields  $Z_{\alpha,p}^{\pi} = 0.091$  (summed over the para and two ortho positions) and allows us to compare a cyclopropyl, phenyl, and vinyl group. The indexes reveal that these three moieties have nearly equal abilities to induce charge separation in an adjacent carbonyl unit. Presumably, this would correlate with their capability to stabilize an adjacent positive charge and, indeed, when properly positioned, these three residues do have similar abilities, which are greatly enhanced as compared to the analogous saturated systems.<sup>30</sup>

One further non-enonic system investigated was the homoconjugated molecule norborn-5-en-2-one. In this example,  $Z_{\gamma}^{\pi}$  was found equal to 0.042, considerably reduced, as expected for this type of  $\beta, \gamma$  interaction.

So far, we have discussed only the  $\beta$ -carbon atom, which, according to resonance theory, should bear a partial positive charge. This same theory suggests that  $C_{\alpha}$  should remain neutral, while more advanced treatments reveal that the  $\alpha$ -carbon atom should bear a negative charge, the magnitude of which depends upon the theoretical method employed, but is always smaller than the density magnitude at  $C_{\beta}$ .<sup>11</sup> Perhaps resonance theory is indicating that  $Z_{\alpha}^{\pi}$  should be simply less sensitive to substituents than  $Z_{\beta}^{\pi}$ . In an attempt to further test our procedure, we have calculated  $Z_{\alpha}^{\pi}$  for all of the above systems where possible. The results are presented in Table II. It was gratifying to find that in every case examined,  $Z_{\alpha}^{\pi}$  was negative or very close to zero and generally smaller than the associated  $Z_{\beta}^{\pi}$  index. Furthermore, a statistical analysis revealed that  $Z_{\alpha}^{\pi}$  varies over a much narrower range than the corresponding  $Z_{\beta}^{\pi}$  values. Time has not yet permitted a more detailed analysis of these variations in  $Z_{\alpha}^{\pi}$ .

All of the  $Z^{\pi}$  indexes discussed above appear to fit into an order which is consistent with expectation. However, further corroboration as well as an analysis of the absolute accuracy of these results seems desirable. In order to comment upon this latter aspect we have collected, in Table IV, the  $\pi$  electron density at the  $\beta$ -carbon atom in *s-trans*-acrolein as calculated

Table V. Comparison of Some Computed and Experimental Charge Densities

| Compound                           | $Z_{\beta}^{\pi}$ (exp) | $Z_{\beta}^{\pi}$ (CNDO)                                  |
|------------------------------------|-------------------------|---|
| Cyclopentadienone                  | 0.111                   | 0.00 <sup>23</sup>  |
| Methyl vinyl ketone                | 0.090                   | 0.045 <sup>11b</sup>                                      |
| Acetophenone                       | 0.091                   | 0.059 <sup>32</sup>                                       |
| Cyclohexenone                      | 0.097                   | 0.069 <sup>11b</sup>                                      |
| <i>trans</i> -Pent-3-en-2-one      | 0.104                   | 0.07-0.09 <sup>11b</sup>                                  |
| 4-Methylpent-3-en-2-one            | 0.114                   | 0.086 <sup>3e</sup>                                       |
| Acrolein                           | 0.135                   | 0.047 <sup>11b</sup>                                      |
| Tropone                            | 0.175                   | 0.18 <sup>23</sup>  |
| Di- <i>n</i> -propylcyclopropenone | 0.393                   | 0.33 <sup>23</sup> (di- <i>tert</i> -butylcyclopropenone) |

by a variety of MO techniques. These data seem to indicate that our method probably overestimates  $\pi$  electron densities. However, these calculations have not taken effects, such as those created by the solvent, explicitly into account. Such factors would be expected to lead to a considerable increase in charge polarization.

In regards to further substantiation of the relative trends observed, we sought to compare our  $Z_{\beta}^{\pi}$  indexes with available calculated  $\pi$ -electron densities. As Table IV reveals, these computed charge densities are highly dependent upon the MO technique employed. In order to ensure, as best as possible, that the observed computational trends would be meaningful, we have limited our comparison to CNDO derived results. The data contained in Table V illustrate that a crude correlation does exist between the two limited sets of data.

## Conclusions

A simple empirical procedure has been advanced which correlates <sup>13</sup>C NMR shift differences in unsaturated carbonyl containing compounds with relative  $\pi$  electron densities (as estimated via calculations or relative cation stability). As discussed above, <sup>13</sup>C NMR chemical shifts should be influenced by charge densities; however, other elements of the chemical shift tensor are also expected to make contributions. Judging by the reasonable  $Z^{\pi}$  indexes obtained, we must conclude that, at least within the series of compounds examined, these additional factors remain essentially constant or else fortuitously cancel.

Not only does this method provide a relatively accurate and readily understood electronic description of the molecule, but it also allows for the facile identification of anomalies and trends (for example, the dual effects of conformation and internuclear separation in the cycloalkenone series). All of these results serve to strengthen our belief that this method, after further verification, may provide chemists with a routine method for the rapid collection and evaluation of significant molecular information.

## Experimental Section

All <sup>13</sup>C NMR spectra were recorded on a Varian XL-100-15 spectrometer operated in the Fourier transform (FT) mode. A spectral width of 3000-7000 Hz was typically employed, allowing a chemical shift accuracy better than  $\pm 0.05$  ppm to be obtained. Spectra were routinely recorded as ca. 1.0 M solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si serving as an internal standard. Signal assignments were based on model compounds, off-resonance decoupling, single proton decoupling, LIS, and intensity studies, as well as selective deuteration. Samples were not degassed nor run under any other special conditions unless noted.

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## $\gamma$ -Chloroallyl Sulfoxides as Latent $\alpha,\beta$ -Unsaturated Carbonyl Compounds. A New Approach to Steroid Synthesis

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**Abstract:**  $\gamma$ -Chloroallyl sulfoxides undergo [2,3] sigmatropic rearrangement and "self-immolative" fragmentation of  $\alpha$ -chloro sulfenates with great ease.  $\alpha,\beta$ -Unsaturated carbonyl compounds with varying substitution patterns can thus be generated at an appropriate stage of a multistep synthesis. The approach is illustrated with construction of potential steroid precursors 17 and 18.

Chloro olefin annelation has proven to be versatile for construction of five- through seven-membered carbocyclic rings, especially in the steroid and terpene areas.<sup>1</sup> Likewise, chloroalkene units can be successfully employed in electrocyclic reactions proceeding via cyclic transition states, but not resulting directly in ring formation ("chloro olefin pseudo-annelation").<sup>2,3</sup> Thus, [3,3] sigmatropic alkylations employing  $\beta$ -chloroallyl vinyl ethers played a key role in hirsutane synthesis,<sup>2</sup> while exploratory [2,3] sigmatropic rearrangements of  $\gamma$ -chloroallyl sulfoxides and amine oxides, followed by further decomposition (vide infra), indicated their capabilities as latent  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>3</sup>

The present paper concerns potential applications of  $\gamma$ -chloroallyl sulfoxide rearrangements to steroid synthesis. Related synthetic utilization of allyl sulfoxide-sulfenate equilibria<sup>4</sup> involve thiophile-assisted conversions of sulfenates

into allyl alcohols.<sup>5</sup> Regiospecific generation of synthetically versatile  $\alpha,\beta$ -unsaturated ketones from latent precursors, as we discuss herein, complements extensive recent work of others on enone synthesis. Some examples are 1,3-alkylative carbonyl transposition,<sup>6</sup> alkylative elimination of  $\alpha$ -sulfinyl esters,<sup>7</sup> and introduction of  $\alpha,\beta$ -unsaturation into existing ketones<sup>8a,b</sup> and esters<sup>8c</sup> via selenoxide eliminations.

From the outset of our studies with  $\gamma$ -chloroallyl sulfoxides,<sup>3</sup> it was clear that such species would in some cases rearrange so rapidly that deprotonation and alkylation prior to "self-immolative" rearrangement-elimination<sup>9</sup> might be problematic. Thus, sulfoxide **1**<sup>10</sup> can be methylated and the crude **1a** (estimated yield ca. 65%) completely transformed during 2 h of refluxing in carbon tetrachloride-cyclohexene to *trans*-3-pentene-2-one (**2**) and the phenylsulfenyl chloride adduct **3** (Scheme I). However, **1a** and comparably alkylated