

Proton Magnetic Resonance Spectra and Electronic Effects in Substituted 1,3-Diketones

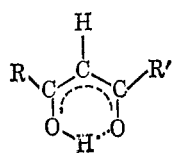
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Abstract: The nuclear magnetic resonance spectra of nine 1,3-diketones have been recorded. Particular attention is paid to the position of the methylene and enolic resonance peaks with respect to the electronic effects of the groups substituted at the 1 or 3 position. The series studied consists of combinations of trifluoromethyl, methyl, phenyl, and 2-thienyl groups substituted at the 1 and 3 positions. Interpretation of peak shifts within the series leads to the conclusion that, relative to 2,4-pentanedione, the trifluoromethyl group is electron withdrawing by induction while the phenyl and 2-thienyl groups are electron releasing by resonance. Interpretation of the infrared spectra of the copper(II) chelates of these 1,3-diketones results in the same conclusions as to the electronic effect of the substituents when substituted in a chelate ring.

The electronic effects of replacing the methyl groups on 2,4-pentanedione with trifluoromethyl, phenyl, or 2-thienyl groups have been studied with proton magnetic resonance spectroscopy. Nakamoto, Morimoto, and Martell² have earlier studied the electronic effects of the trifluoromethyl and phenyl groups on the copper(II) 1,3-diketone chelates by means of infrared spectroscopy. In their work, the bond strengths of the C=C, C=O, and O—Cu bonds are discussed in relation to the electronic effect of the substituent groups. The work reported herein relates the proton magnetic resonance chemical shifts of the methylene proton and the enolic proton to the electronic effect produced by the substituent groups. Both the infrared study and the proton magnetic resonance study show the ability of the trifluoromethyl group to attract electron density from the enolic or chelate ring by induction. Both studies also show the ability of the aromatic substituents to supply electron density to the chelate or enolic ring by resonance.

The compounds studied in this paper are represented by the formula



where R and R' = CF₃, CH₃, C₆H₅, or 2C₄H₃S. The chemical shifts of the methylene proton and of the enolic proton are each sensitive to the electronic effects of the substituent groups R and R'.

Experimental Section

Proton Magnetic Resonance Spectral Measurements. A Varian A-60 nuclear magnetic resonance spectrophotometer was used to obtain the spectra. All samples were run in carbon tetrachloride. Sample concentration was 10% by weight. The chemical shift of all resonance peaks is compared to tetramethylsilane ($\delta = 0$ ppm) as the internal standard.

Infrared Spectral Measurements. Infrared spectra in the 1300- to 400-cm⁻¹ range were recorded using Nujol mulls between potassium bromide plates.³ Spectra were recorded in the 2000- to

625-cm⁻¹ range using potassium bromide pellets. Infrared peaks for the spectra of compounds common to the series reported here and the series of Nakamoto, *et al.*,² agree to within ± 5 cm⁻¹.

Preparation of Compounds. The following compounds were obtained from commercial sources: 2,4-pentanedione, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, and 1,1,1-trifluoro-4(2-thienyl)-2,4-butanedione. The following compounds were prepared by methods reported in the literature:⁴ 1,1,1-trifluoro-4-phenyl-2,4-butanedione, 1(2-thienyl)-1,3-butanedione, and 1,3-di(2-thienyl)-1,3-propanedione. The compounds purchased commercially were the highest purity available. The compounds which were prepared in our laboratories had melting points which were in very good agreement with values in the literature. In no case did the spectra of these compounds show any proton magnetic resonance peaks which were unexplained or which could be attributed to impurities.

Results and Discussion

The proton magnetic resonance spectra were determined for nine 1,3-diketones which were substituted at the 1 or 3 position with CH₃, CF₃, C₆H₅, or 2C₄H₃S. The chemical shifts of the methylene and enolic protons in these compounds are listed in Table I.

Table I. Proton Magnetic Resonance Chemical Shifts of Methylene and Enolic Protons in Some Substituted β -Diketones (δ , ppm vs. TMS)

Compd	R	R'	Methylene proton chemical shift, δ (ppm)	Enolic proton chemical shift, δ (ppm)
I	CH ₃	CH ₃	5.44	15.40
II	CH ₃	CF ₃	5.90	14.24
III	CF ₃	CF ₃	6.43	13.00
IV	C ₆ H ₅	C ₆ H ₅	6.80	17.13
V	CH ₃	C ₆ H ₅	6.08	16.24
VI	CF ₃	C ₆ H ₅	6.56	15.23
VII	2C ₄ H ₃ S	2C ₄ H ₃ S	6.50	16.2
VIII	CH ₃	2C ₄ H ₃ S	5.93	15.66
IX	CF ₃	2C ₄ H ₃ S	6.42	14.92

1. The Trifluoromethyl Group. Pronounced shifts in the position of the magnetic resonance peaks for the methylene and enolic protons take place when the methyl groups in 2,4-pentanedione are replaced with trifluoromethyl groups. The enolic resonance peak is

Co., Midland, Mich., who recorded the infrared spectra of the copper chelates in the 1300- to 400-cm⁻¹ range.

(4) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

(1) Dow Research Fellow, 1964-1965, and Du Pont Teaching Fellow, 1965-1966, University of Nebraska.

(2) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

(3) Appreciation is expressed to Dr. H. David Russell, Dow Chemical

shifted upfield by about 1.2 ppm for each trifluoromethyl group that is added. Thus, the trifluoromethyl group can be considered as increasing the shielding of the enolic proton nucleus. The strong electron withdrawal due to the inductive effect of the trifluoromethyl group would be expected to strengthen the C=O bond at the expense of the O—H bond. For this reason, the enolic proton is shielded to a greater extent by its own electron cloud in the trifluoro and hexafluoro compounds than in 2,4-pentanedione. This interpretation is consistent with the acidities of the three 1,3-diketones (I, II, and III). According to Van Uitert⁵ the pK_a values are for I, 12.7; II, 8.7; and III, 6.0. The trend in acidity in going from I to II to III indicates a weakening of the O—H bond due to the inductive effect of the trifluoromethyl group.

The methylene proton magnetic resonance peak is shifted downfield by about 0.5 ppm for each trifluoromethyl group substituted on 2,4-pentanedione. This deshielding of the methylene proton can also be explained by the inductive effect of the trifluoromethyl group. This group would be expected to strengthen the C=C bond in the enolic ring. The strengthening of the C=C bond decreases the electronic shielding of the methylene proton.

Nakamoto, Morimoto, and Martell² have studied the infrared spectra of the copper(II) chelates of compounds I, II, and III in order to determine the electronic effect of the trifluoromethyl group. They interpreted an increase in the stretching frequencies of the C=C and C=O bonds for the series bis(2,4-pentanedionato)copper(II), bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II), and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) as due to increased bond strength arising from inductive effects. The expected weakening of the Cu—O bond was indicated by a decrease in the Cu—O stretching frequency when trifluoromethyl groups are substituted for methyl groups. Both the proton magnetic resonance spectra and infrared spectra of the trifluoromethyl derivatives can be explained by the inductive electron withdrawal of the CF_3 group.

2. The Phenyl Group. Replacing the methyl groups in 2,4-pentanedione with phenyl groups also results in shifts of the magnetic resonance peaks for the methylene and enolic protons. Phenyl substitution at the 2 or 4 position in 2,4-pentanedione produces a downfield shift of the enolic proton resonance peak. The shift is about 0.86 ppm for each phenyl group added. The most significant fact about this shift is that the phenyl group causes a deshielding of the enolic proton, whereas the trifluoromethyl group increases the shielding of the enolic proton nucleus. The deshielding of the enolic proton nucleus can be explained by assuming the phenyl group supplies electron density to the enolic ring through resonance. The resonance weakens the C=O bond and strengthens the O—H bond by increasing the electron density on the oxygen. The increased electron density on the oxygen deshields the enolic hydrogen, a phenomenon manifested in the downfield shift of the enolic hydrogen resonance peak. The potentiometrically determined dissociation constants measured by Van Uitert⁵ also indicate that the O—H

bond is strengthened by phenyl substitution: I, $pK_a = 12.7$; V, $pK_a = 12.9$; and IV, $pK_a = 13.8$. This interpretation of the electronic effect of the phenyl group on the C=O and O—H bonds is supported by the infrared study of Nakamoto, Morimoto, and Martell.² They state that the effect of substituting phenyl groups for methyl groups in bis(2,4-pentanedionato)copper(II) is a weakening of the C=O bond and a strengthening of the Cu—O bond. They attribute this effect to resonance of the phenyl group with the chelate ring. Burdett and Rogers⁶ have stated that the phenyl and enolic rings cannot be coplanar and therefore that resonance is not a factor in these phenyl-substituted 1,3-diketones. However, the deshielding of the enolic hydrogen that results from phenyl substitution together with pK_a data and infrared spectra appears to show the importance of a resonance effect.

Phenyl substitution on 2,4-pentanedione also results in a downfield shift of the methylene hydrogen resonance peak. Each additional phenyl group shifts the peak 0.6 to 0.7 ppm downfield. This methylene resonance peak shift may be attributed to a number of phenomena. It may be caused by inductive effects as believed by Burdett and Rogers.⁶ The shift might also be caused by the long range anisotropic effect of the phenyl ring. A third possibility is electron release of the phenyl group by resonance. The latter explanation seems the most plausible in light of additional data discussed below. Nakamoto, Morimoto, and Martell² observed a shift to higher frequencies for the C=C bond in the infrared spectra of the copper(II) chelates when the methyl groups are replaced by phenyl groups. Their perturbation calculations also lead to the conclusion that phenyl substitution increases the strength of the C=C bond. The downfield shift of the methylene proton magnetic resonance peak is consistent with this explanation.

The possibility still exists that the methylene proton peak shift may be due to the anisotropic effect of the phenyl ring. Assuming that the phenyl group is indeed coplanar with the enolic ring, the methylene proton is probably in the plane of the phenyl ring. Thus, an anisotropic effect should deshield the methylene proton. This effect is observed. However, the infrared results discussed above leave little doubt that the C=C bond is strengthened, which would also result in deshielding the methylene proton. Thus, it appears that the downfield shift of the methylene proton is caused by C=C bond strengthening due to resonance and is reinforced by long range anisotropic effects. Inductive effects of the phenyl group have been ruled out in light of the above discussion concerning the peak shifts of the enolic resonance peak.

3. The 2-Thienyl Group. Substitution for the methyl groups in 2,4-pentanedione by 2-thienyl groups results in proton magnetic resonance spectra that are quite similar to those obtained for the phenyl-substituted compounds. The differences are not in the direction of the methylene and enolic hydrogen peak shifts, but only in the degree of the shifts. Thienyl substitution shifts the methylene proton resonance peak downfield about 0.5 ppm for each group added. Presumably it affects the methylene proton in the same way the phenyl group does (that is, by resonance and aniso-

(5) L. G. Van Uitert, Ph.D. Thesis, Pennsylvania State College, 1952, and L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

(6) J. L. Burdett and M. T. Rogers, *ibid.*, **86**, 2105 (1964).

Table II. Infrared Absorption Peaks (cm^{-1}) of 2-Thienyl-Substituted 1,3-Diketone Copper(II) Chelates

Substituents		ν_8	ν_1	ν_5
R	R'	(C=C Stretch)	(C=O Stretch)	(Cu—O Stretch)
CH ₃	CH ₃	1580	{1548 1524}	455
CH ₃	2C ₄ H ₃ S	1569	1530	460
2C ₄ H ₃ S	2C ₄ H ₃ S	1535	1520	468

tropic effects), but to a lesser degree. Here again, inductive effects seem to be ruled out because of observed shifts in the enolic proton resonance peak.

Thienyl substitution shifts the enolic proton resonance peak downfield from about 0.3 to 0.5 ppm for each group substituted. The direction of the enolic peak shift is opposite to that observed in the trifluoromethyl-substituted compounds and in the same direction as in the phenyl-substituted derivatives. Hence, the thienyl group is assumed to cause a weakening of the C=O bond and a strengthening of the O—H bond by resonance. The effect, however, is significantly less than is observed in the phenyl-substituted compounds. This is a consequence of the fact that 2-thienyl is a weaker electron-releasing group by resonance than the phenyl group. The potentiometrically determined dissociation constants of the thienyl derivatives do not appear to be as good a measure of O—H bond strengthening as they were in the case of the phenyl-substituted compounds. The $\text{p}K_{\text{d}}$ values measured by Van Uitert⁵ are as follows: I, $\text{p}K_{\text{d}} = 12.7$; VIII, $\text{p}K_{\text{d}} = 12.4$; VII, $\text{p}K_{\text{d}} = 12.6$.

The infrared spectra of the 2-thienyl-substituted compounds were recorded and peaks were assigned in a similar manner to that of Nakomoto, *et al.*² (see Table II).

The infrared data show the expected decrease in the C=O stretching frequency and increase in the Cu—O stretching frequency when 2-thienyl groups are substituted for methyl groups. Inasmuch as such changes in frequency indicate C=O bond weakening and Cu—O bond strengthening, the effect of the 2-thienyl group is assumed to be electron release to the chelate ring by resonance.

In the discussion of the proton magnetic resonance spectra, it was assumed that the deshielding of the methylene proton in the 2-thienyl derivatives was caused by C=C bond strengthening in a manner similar to that for the phenyl derivatives. The decrease in the infrared C=C stretching frequency (*i.e.*, an indication of decreased bond strength) is puzzling in view of the proton magnetic resonance data and the fact that CF₃ and C₆H₅ groups both increase the strength of this bond. All three groups have much the same effect on the methylene proton magnetic resonance peak in the unchelated 1,3-diketone. It appears that the electronic effect of the thienyl group affects the C=C bond of the copper(II) chelate ring in a different manner than either the CF₃ group or the C₆H₅ group. The thienyl group does, however, strengthen the Cu—O bond just as does the phenyl group.

4. Aromatic and Trifluoromethyl-Substituted Compounds. The aromatic trifluoromethyl compounds (VI and IX) can be considered as intermediate between the diaromatic compounds (IV and VII) and 1,1,1,5,5,5-

Table III. Infrared Absorption Peaks (cm^{-1}) of Some Unsymmetric Trifluoromethyl Copper(II) Chelates of 1,3-Diketones

Substituents		ν_8	ν_1	ν_5
R	R'	(C=C Stretch)	(C=O Stretch)	(Cu—O Stretch)
CH ₃	CF ₃	1611	1600	445
C ₆ H ₅	CF ₃	1601	1575	444
2C ₄ H ₃ S	CF ₃	1596	1575	459

hexafluoro-2,4-pentanedione (III). The methylene protons in the aromatic trifluoromethyl compounds are deshielded to about the same extent as the symmetric diaromatic compounds and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Presumably, the deshielding results from the inductive effect of the trifluoromethyl group and the resonance effect of the aromatic group, both of which have been shown to deshield the methylene proton. The C=C bond in the unsymmetrically substituted trifluoromethyl copper chelates is strengthened in every case relative to the copper chelate of 2,4-pentanedione. This is shown by the increased frequency of absorption for the C=C bond stretching mode in the series given in Table III. Assignments in Table III were made in a similar manner to that of Nakomoto, *et al.*² Thus, proton magnetic resonance of the unchelated 1,3-diketone and infrared spectra of the corresponding copper chelates support the conclusion that the net effect of the substituents in these compounds is to strengthen the C=C bond and thereby deshield the methylene proton.

The chemical shift of the enolic proton depends upon the resultant effect of the trifluoromethyl group and the other substituent group on the enolic ring. For compound VI the resonance peak of the enolic proton is just slightly upfield from the enolic proton peak in 2,4-pentanedione. Thus it appears that the weakening of the O—H bond by the trifluoromethyl group is slightly more important than the strengthening of the O—H bond by the phenyl group. Infrared data also support this interpretation. In proceeding from bis(2,4-pentanedionato)copper(II) to bis(1,1,1-trifluoro-4-phenyl-2,4-butanedionato)copper(II) there is a strengthening of the C=O bond (1548 *vs.* 1575 cm^{-1}) and a weakening of the Cu—O bond (455 *vs.* 444 cm^{-1}). In compound IX, the enolic proton resonance peak is found about 0.5 ppm upfield as compared to the position of the peak in 2,4-pentanedione. The increased shielding of the enolic proton in compound IX must be due to the strong inductive effect of the trifluoromethyl group and the relatively weak resonance effect of the 2-thienyl group. Infrared spectra show the expected strengthening of the C=O bond in going from bis(2,4-pentanedionato)copper(II) to bis(1,1,1-trifluoro-4(2-thienyl)-2,4-butanedionato)copper(II); however, the Cu—O bond does not appear to be weakened. This peculiar behavior of the Cu—O bond points out once again the puzzling nature of the infrared data for the 2-thienyl-substituted copper(II) chelates.

In Figures 1 and 2, the methylene proton chemical shift is plotted *vs.* the enolic proton chemical shift. In Figure 1 the six compounds representing the various combinations of CH₃, CF₃, and C₆H₅ substitution are plotted. In Figure 2, the six compounds resulting from CH₃, CF₃, and 2C₄H₃S substitution are similarly

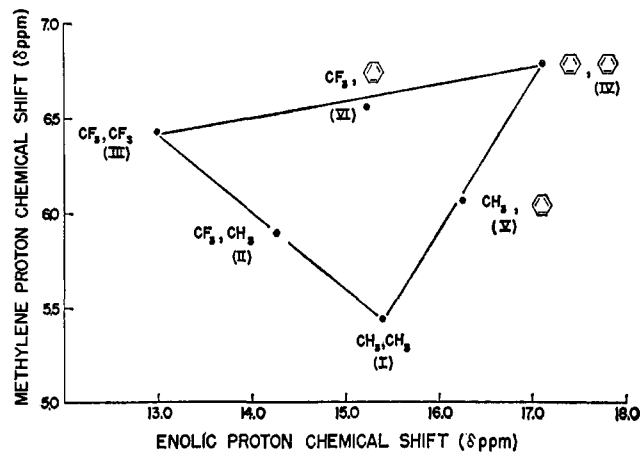


Figure 1. Methylene proton chemical shift vs. enolic proton chemical shift for 1,3-diketones with CF_3 , CH_3 , and C_6H_5 substituted in the 1 and 3 positions.

plotted. The triangular diagrams that result have some interesting aspects that are worthy of mention. In Figure 1, the slope of the line from 2,4-pentanedione (I) to the diphenyl derivative (IV) is positive due to the deshielding of both the methylene and enolic protons by the phenyl group. In the discussion above, this has been attributed to the effect of resonance of the $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{O}-\text{H}$ bonds in the enolic ring. The same reasoning accounts for the positive slope of the line in Figure 2 from compound I to VIII to VII. In Figure 2, the positive slope reflects the resonance effect of the 2-thienyl group on the $\text{C}=\text{C}$, $\text{C}=\text{O}$, and $\text{O}-\text{H}$ bonds. The line for the 2-thienyl derivatives in Figure 2 has a more positive slope than the line for the phenyl derivatives in Figure 1. This seems reasonable inasmuch as the weak electron-releasing ability of the 2-thienyl group might be expected to deshield the enolic proton to a lesser extent than does the phenyl group.

The negative slope for the line from 2,4-pentanedione to 1,1,1,5,5,5-hexafluoro-2,4-pentanedione can be explained by the inductive effect of the trifluoromethyl group. It results from the inductive strengthening of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds in the enolic ring. This

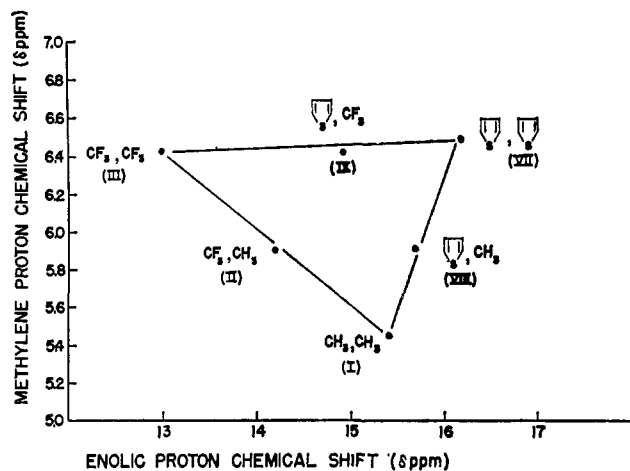


Figure 2. Methylene proton chemical shift vs. enolic proton chemical shift for 1,3-diketones with CF_3 , CH_3 , and $2\text{C}_4\text{H}_3\text{S}$ substituted in the 1 and 3 positions.

bond strengthening deshields the methylene proton and shields the enolic proton, relative to 2,4-pentanedione.

Thus, the empirical figures serve to illustrate the electronic effect of the substituent as compared to 2,4-pentanedione. A positive slope indicates electron release to the enolic ring whereas a negative slope indicates electron withdrawal from the enolic ring. Furthermore, the relative value of the slope appears to provide a qualitative measure of the strength of the substituent's electronic effect.

Nakamoto, *et al.*,² have correlated the $\text{Cu}-\text{O}$ stretching frequency, which occurs at about 450 cm^{-1} , to the stability of these copper(II) chelates. Lintvedt and Holtzclaw⁷ have reported a correlation between the chemical shift of the enolic hydrogen in the unchelated 1,3-diketone and the stability of the 1,3-diketone chelates. Thus, the good correlation between the chemical shift of the 1,3-diketone enolic hydrogen and the stretching frequency of the metal-oxygen bond is not surprising. Both infrared and proton magnetic resonance data may be used as spectral measures of chelate stability.

(7) R. L. Lintvedt and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 239 (1966).