σ–π CONJUGATION*†: OCCURRENCE AND MAGNITUDE

T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall

Chemistry Department, Revelle College, University of California, San Diego, La Jolla, California

ABSTRACT

Charge-transfer spectra of aryl-CR_2-Metal$(X)_n$ systems have been used to study the nature and extent of C–Metal hyperconjugation. Effects of changes in X, changes in R, and changes of the metal (C, Si, Ge, Sn, Pb, Hg, B, etc.) on the extent of σ–π conjugation as well as effects of rotation about the aryl–C bond have been determined. The dependence of σ–π conjugation upon electron deficiency is discussed and a general theory for the extent of hyperconjugation is presented.

Hyperconjugation or σ–π conjugation has been controversial since it was first proposed, possibly because the two observations which it was proposed to explain, shortened single bonds[1] and effects of alkyl groups on aromatic reactivity[5, 6], proved to be due to other effects[7, 8, 9]. Despite these setbacks and a continual abandonment of the idea in favour of other concepts such as bridging[10], fragmentation[11], d-orbital participation[12], σ–π conjugation remains a viable and demonstrable effect for electron-deficient species[13h].

This paper briefly summarizes our efforts to demonstrate and to probe the magnitude and geometrical requirement of σ–π conjugation as a function of structure of electron-deficient species, with special emphasis on C–Metal σ–π conjugation. Other species are discussed elsewhere[13h].

To illustrate our use of the term σ–π conjugation (or σ–π delocalization) we show below (*Figure 1*), with valence bond representations, the delocalization of several types of electron pairs into a p-orbital.

We refer to all these conjugation effects as 'vertical stabilizations' of the cation because they reveal themselves in vertical processes[13a].

The quantum mechanical description of σ–π conjugation, after Mulliken[4],

π–π Conjugation

(I)

n–π Conjugation

(II)

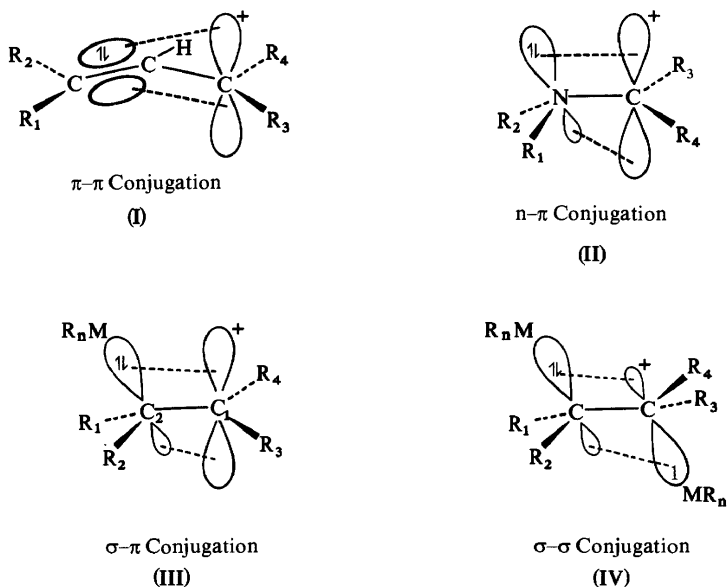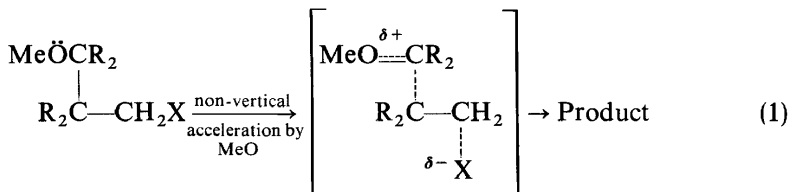σ–π Conjugation

(III)

σ–σ Conjugation

(IV)

Figure 1. Examples of conjugation: delocalization of electron pairs into cation centres

begins with the species (III) in which the R_nMC- is tetrahedral and has normal bond lengths, the $\overset{+}{C}R_3R_4$ is trigonal planar, and the C—C bond length is normal for an sp²–sp³ σ-bond. We might then calculate the energy of the system with and without the C_1—C_2 π-overlap and call the difference the σ–π conjugation energy.

Movement of the groups M, R_1 and R_2 which are required for this stabilization we have called 'non-vertical stabilization' and we will not include this in our definition of σ–π conjugation[13a, k]. For example, we have shown elsewhere that frangomeric acceleration is a non-vertical process and the stabilization providing this acceleration is not detectable in vertical ionization processes[131].

$$
\begin{matrix} \text{MeÖCR}_2 \\ | \\ \text{R}_2\text{C—CH}_2\text{X} \end{matrix}
\xrightarrow[\substack{\text{acceleration by} \\ \text{MeO}}]{\text{non-vertical}}
\left[
\begin{matrix} \text{MeO} \overset{\delta+}{\cdots} \text{CR}_2 \\ \vdots \\ \text{R}_2\text{C—CH}_2 \\ \vdots \\ \overset{\delta-}{} \text{X} \end{matrix}
\right]
\rightarrow \text{Product} \qquad (1)
$$

It is important to differentiate elimination *processes* which Nesmeyanov[2] has called σ–π transformations from σ–π conjugation[1]. The term σ–π transformation implies nuclear movement which is non-vertical whereas σ–π conjugation is electron delocalization and is a vertical stabilization like that of n–π conjugation. More accurately, we should say that σ–π conjuga-

600

tion is as vertical as n–π conjugation because our definition is an empirical one based upon this comparison.

Methods of estimating vertical stabilization

We have used ionization potentials of olefins or aromatic compounds to probe the vertical effect of an M—C σ-bond (Y = − CR_2M) upon a positively charged carbon.

$$(2)$$

It is well established that ionization potentials of mono-substituted benzenes follow the Hammett equation[14, 15]

$$\text{Ionization Potential (eV)} = 1.31\ \sigma^+ + 9.24 \qquad (3)$$

or in terms of charge-transfer frequencies of benzenes with tetracyanoethylene in methylene chloride, follow the equation[13a]:

$$v_{CT}\,(\text{cm}^{-1}) = 9\,300\,\sigma^+ + 26\,200 \qquad (4)$$

As a calibration of the size of the effect of Y on chemical reactions, consider the reaction[13d]

$$(5)$$
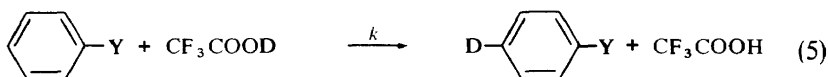
where a change in σ^+ of one unit (corresponding to changing v_{CT} by 9 300 cm^{-1} or I.P. by 1.31 eV) changes the rate by a factor of 10^8.

Magnitude of σ–π conjugation

The following table lists the charge-transfer frequencies of a few benzyl metal compounds which illustrate just how large the effect can be

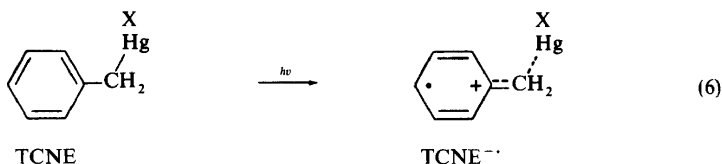Table 1. Charge-transfer frequencies of Ph—Y compounds with tetra-cyanoethylene in methylene chloride and the derived σ_Y^+ constants

Ph—Y	$v\,(\text{cm}^{-1})$	σ_Y^+
Ph—H	25 840	(0.0)
Ph—CH$_3$	24 330	−0.2
PhCH$_2$CPh$_3$	23 700	~(−0.2)*
PhCH$_2$SiPh$_3$	22 220	−0·42
PhCH$_2$GePh$_3$	20 660	−0.60
PhCH$_2$SnPh$_3$	18 760	−0.81
PhCH$_2$PbPh$_3$	17 060	−1.0
PhCH$_2$SnMe$_3$	(26 700)†	−0.91
PhCH$_2$HgC$_6$H$_{11}$	(24 150)†	−1.2
PhCH$_2$CH$_2$PbPh$_3$	24 700	(−0.16)*

* These are maximum negative values. The tetracyanomethylene could be complexing with the wrong phenyl group. This problem does not arise in the PhCH$_2$MPh$_3$ compounds with lower ionization potentials.
† The tetracyanomethylene complex is unstable. These values refer to dichloromaleic anhydride charge-transfer spectra.

The data in this table clearly indicate that σ–π conjugation increases as the metal becomes more electropositive. Notice that the $-CH_2PbPh_3$ group provides enough stabilization for 10^8 rate acceleration in equation 5. However, insertion of one methylene group $(PhCH_2CH_2PbPh_3)$ insulates the σ–π conjugation removing the effect of the $-PbPh_3$ group completely[13a].

We have also shown that changes in the metal substituent (X) have a very large inductive effect upon this conjugation[13j].

$$\nu_{TCNE}^{PhCH_2HgX} = 11\,200\,\sigma_X^I + 15\,700 \tag{7}$$

Compare this effect (slope and intercept) with the much smaller effect of CH_2X
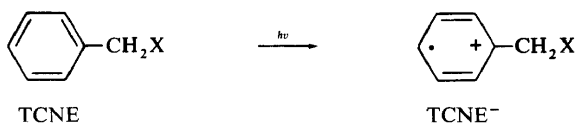
$$\nu_{TCNE}^{PhCH_2X} = 4\,300\,\sigma_X^I + 24\,250 \tag{9}$$

Notice also the inductive order of the charge-transfer frequencies of $-CH_2M(CH_3)_n$ versus $-CH_2MPh_n$ in *Table 1*.

Stereoelectronic effects

The most spectacular demonstration of the requirement that the C—M σ-bond be parallel to the aromatic system is shown in *Table 2*.

*Table 2.* Charge-transfer frequencies of organometallic and related compounds*†

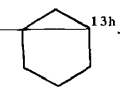| Structure Y		H_2C—Y
—H	23 600	24 300
—Sn(CH$_3$)$_3$	23 600	17 500
—HgC$_6$H$_{11}$	24 000	15 000

* Conditions given in *Table 1*.
† Part of this table appears in reference 13j.

Notice that the substitution of $-HgC_6H_{11}$ for H in $PhCH_2Y$ changes the frequency by $9\,300$ cm^{-1} or 10^8 change in the rate of reaction! However, this same substitution in the benzyl position of the bicyclic system is without effect. Rotating the σ-bond 90° turns off an effect equivalent to 10^8 in rate!! This is a very large and stereoelectronically rigid resonance effect[16].

The effect of changes in the hyperconjugated group may be summarized in the following sequence of effects on the ionization potentials of $PhCH_2R$

$$R = H < CX_3^a < SiX_3^b < GeX_3^b < SnX_3^b < PbX_3^b \sim HgX^b < CdR \text{ etc.}$$
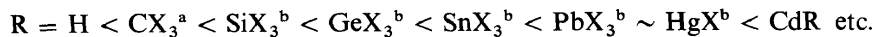
a. Resonance stabilization of $\overset{+}{C}X_3$ is not important here, but inductive effects are. Thus $CMe_3 > CPh_3$ as hyperconjugating group. However σ–π conjugation of C—C σ-bonds

can be very large if the bond is strained as in Ph—[13h].

b. Resonance effects in X are also absent in C–Metal conjugation. However, inductive effects are very large. For example, R = HgBr and R = $SiMe_3$ give about the same amount of σ–π conjugation. Strain in the C–Metal bond should also increase electron donation just as in the case of strained C—C bonds.

Hydride abstraction and σ–π conjugation

A perusal of the σ^+ values in *Table 1* reveals that many of these CH_2M groups are as stabilizing as MeO towards carbonium ions. But we know from solvolysis data[10] that CH_3OCH_2 is more stable than Ph_3C^+. This means that vertical stabilization by, e.g. the $-CH_2SnMe_3$ groups should be sufficient to make the ion $^+CH_2CH_2SnMe_3$ more stable than the Ph_3C^+ ion.

We have tested this idea by allowing trityl fluoroborate to react with $EtSn(CH_3)_3$ and have discovered a reaction which may have some utility. The reaction follows the stoicheiometry

$$(CH_3)_3SnCH_2CH_3 + Ph_3C^+BF_4^- \rightarrow (CH_3)_3Sn^+BF_4^-$$
$$+ CH_2{=}CH_2 + Ph_3CH \qquad (10)$$
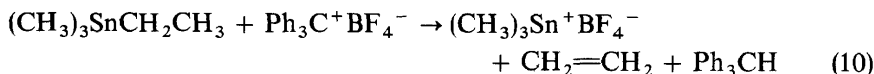
and is first order in each reagent with a second-order rate constant of 1×10^{-2} mol^{-1}s^{-1} at 30°C in acetonitrile. This reaction is quite general for all organometallic compounds having a properly aligned β-hydrogen. Thus Et_2Hg^{17}, Et_4Pb, Et_4Sn, $PhCH(CH_3)SnMe_3$, $PhCH_2CH_2SnMe_3$ all react rapidly to give the olefin. Compounds not having β-hydrogens such as Me_4Pb, $(PhCH_2)_2Hg$, $PhCH_2SnMe_3$, $[PhC(CH_3)_2CH_2]_2Hg$ do not

react. Nor does dicamphylmercury, $\left(-\!\!\!<\!\!\!\underset{}{\overline{}}\!\!\!>\!\!\!-\right)_2$ Hg which is not stereo-

electronically oriented for σ–π conjugation.

Evidence for vertical stabilization in this reaction is seen in the plot of log k_2 for reactions of $HCH_2CH_2M(Et)_n$ against the charge-transfer frequencies of $PhCH_2MPh_n$ in *Figure 2*[13m]. This reaction depends greatly upon the nature of the metal and is well correlated with ionization potentials.

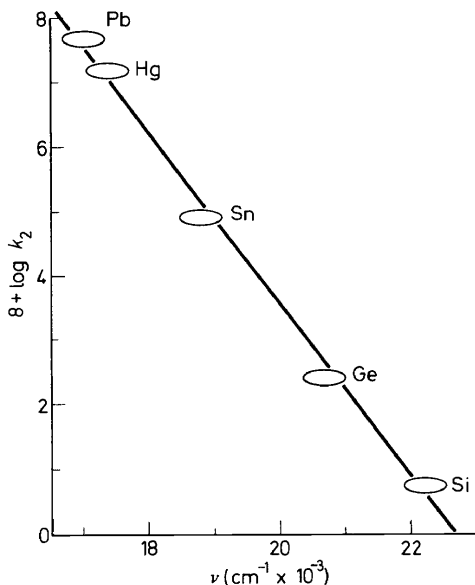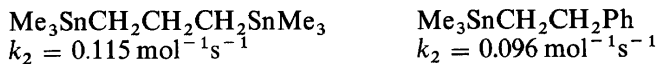*Figure 2.* Plot of log k_2 for hydride abstraction from Et_nM [reaction (10) (30°C, CH_3CN)] against charge-transfer frequencies of Ph_nMCH_2Ph with tetracyanoethylene.
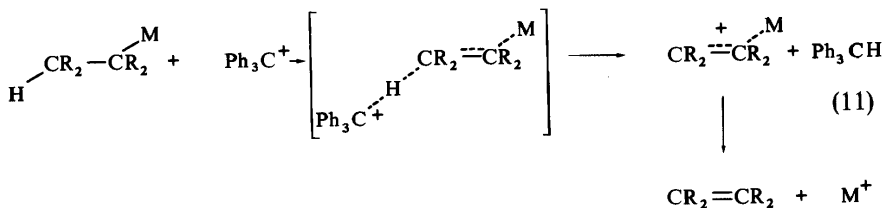
In addition to this correlation, we also notice that a second CH_2SnMe_3 group accelerates the reaction more than does a phenyl group.

$Me_3SnCH_2CH_2CH_2SnMe_3$ $Me_3SnCH_2CH_2Ph$
$k_2 = 0.115 \, mol^{-1}s^{-1}$ $k_2 = 0.096 \, mol^{-1}s^{-1}$

This result leads us to the conclusion that the two Me_3SnCH_2- groups are behaving similarly.
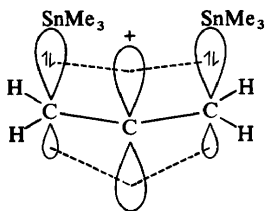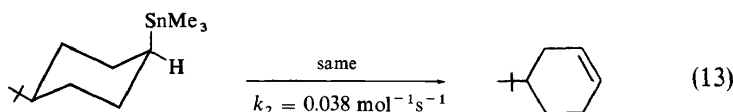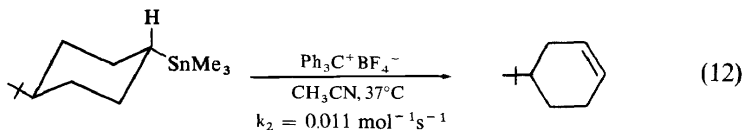

We have therefore written the reaction as

$$(11)$$

in which the transition state is vertically stabilized by σ–π conjugation*.
The stereochemistry of this reaction is shown to be *anti* as indicated in
equation 11 by the following rate comparisons.

$$k_2 = 0.011 \text{ mol}^{-1}\text{s}^{-1} \tag{12}$$

$$k_2 = 0.038 \text{ mol}^{-1}\text{s}^{-1} \tag{13}$$

The faster reaction of the axial-trimethyltin group indicates a preference for
anti elimination which is consistent with deoxymetallation reactions.

REFERENCES

1 A. N. Nesmeyanov and I. F. Lutsenko, *Dokl. Akad. Nauk SSSR*, **59**, 707 (1948).
2 A. N. Nesmeyanov, I. F. Lutsenko, and S. V. Ponomarev, *Dokl. Akad. Nauk SSSR*, **124**, 1073 (1959).
3 (a) R. S. Mulliken, *J. Chem. Phys.* **7**, 339 (1939).
   (b) R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).
4 C. N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.* **80**, 3489 (1958).
5 J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935).
6 J. W. Baker, W. S. Nathan and C. W. Shoppee, *J. Chem. Soc.*, 1847 (1935).
7 M. J. S. Dewar, *Hyperconjugation*, p. 48, Ronald Press, New York (1962).
8 R. A. Alden, J. Kraut and T. G. Traylor, *J. Phys. Chem.* **71**, 2379 (1967); *J. Am. Chem. Soc.* **90**, 74 (1968).
9 W. M. Schubert and D. F. Gurka, *J. Am. Chem. Soc.* **91**, 1443 (1969).
10 See A. Streitwieser, *Solvolytic Displacement Reactions*, p. 103, McGraw-Hill, New York (1962) and P. D. Bartlett, *Nonclassical Ions*, p. 6, Benjamin, New York (1965) for references.
11 C. A. Grob and F. Ostermayer, *Helv. Chim. Acta*, **45**, 1119 (1962).
12 G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. II, p. 211, Methuen, London (1968) and references quoted there.
13 (a) W. Hanstein, H. J. Berwin and T. G. Traylor, *J. Am. Chem. Soc.* **92**, 829 (1970).
   (b) T. G. Traylor and J. C. Ware, *Tetrahedron Letters*, 1295 (1965).
   (c) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.* **89**, 2304 (1967).
   (d) W. Hanstein and T. G. Traylor, *Tetrahedron Letters*, 4451 (1967).
   (e) J. A. Mangravite and T. G. Traylor, *ibid.* 4457 (1967).
   (f) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.* **33**, 2614 (1968).
   (g) T. G. Traylor, *Accounts of Chemical Research*, **2**, 152 (1969).
   (h) N. A. Clinton, R. S. Brown, and T. G. Traylor, *J. Am. Chem. Soc.* **92**, 5228 (1970).
   (i) T. T. Tidwell and T. G. Traylor, *ibid.* **88**, 3442 (1966).
   (j) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.* **92**, 7476 (1970).
   (k) W. Hanstein, unpublished results.
   (l) R. S. Brown, unpublished results.
   (m) J. M. Jerkunica and T. G. Traylor, *J. Am. Soc.* **93**, 6278 (1971).

* This interpretation should be contrasted to the non-vertical stabilization suggested[18, 19]
for similar reactions of ethyl iron compounds in which the acceleration was attributed to π-complex formation.

T. G. TRAYLOR, H. J. BERWIN, J. JERKUNICA, AND M. L. HALL

[14] D. W. Turner, *Advances in Physical Organic Chemistry*, Vol. 4, p. 57, Academic Press, New York (1966).
[15] A. Streitwieser, Jr., *Progress in Physical Organic Chemistry*, Vol. 1, p. 1 Interscience, New York (1963).
[16] See G. G. Pitt, *J. Organomet. Chem.* **23**, C35 (1970) for similar studies.
[17] See O. A. Reutov, E. V. Uglova, V. C. Makhaev and V. S. Petrosyan, *Zh. Org. Khim.* 2153 (1970) for another example of hydride abstraction from R_2Hg.
[18] M. L. H. Green and P. L. I. Nagy, *J. Organomet. Chem.* **2**, 58 (1963).
[19] C. E. Coates, M. L. H. Green, and K. Wade, *Organometallic Chemistry*, Vol. II, p. 216, Methuen, London (1968).