model, I, is inadequate for solvolysis in DMF and DMSO, if we accept that it is a satisfactory model for isomerization in sulfolane. More tentatively we suggest that one of the possible interpretations of Figure 1 is that solvolysis, at least in DMF and DMSO, is an SN2 process in which solvent entry is well advanced on dissociation.

Although solvolysis of the *cis* and *trans* cations leads to the same product, *cis*-$[CoCl(sol)(en)_2]^{2+}$, except in water (*cf.* eq 3 and 4), Figure 1 shows that the transition state for solvolysis of the *trans* cation is a significantly different species from that for solvolysis of the *cis* cation. This conclusion is the same, whether the mechanism is SN1 or SN2.

Experimental Section

All solubilities were measured on analyzed samples.[8,9,12,15,18–21] The crystalline solids were equilibrated by rapid stirring with thermostated solvent for the longest time possible, consistent with their instability in the solvent. The saturated solutions were analyzed spectrophotometrically and reproducibility was ±2%. Solvates were formed with perchlorate salts in dipolar aprotic solvents. The precipitated solid contained solvent which was detected by infrared measurements and could not be removed by exhaustive washing with dry ether. Solvates could not be detected when perchlorates were recrystallized from methanol or water.

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Geometries and Charge Distributions of Organic Ligands. I. Metal–Carbon π Bonding and the Geometry of Acetylene

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received March 11, 1968*

Abstract: The geometrical effects of metal–carbon π bonding on complexed acetylene have been investigated using a model based largely on acetylene intramolecular interactions. The calculations showed that the accumulation of electron density in the π_g orbital through π bonding could lead to either a *cis*- or a *trans*-bent structure, whereas only *cis*-bent structures are observed experimentally. It was found that it was possible to explain this fact in terms of an argument based solely on the symmetry of the metal–acetylene interaction. A similar argument showed that the same forces were also opposed to the *cis* bending of the hydrogen atoms *toward* the metal but had little effect on *cis* bending *away* from the metal.

The nature of the carbon–metal bonding in the transition metal complexes of acetylene has been the subject of considerable speculation. According to the current theory,[1] the carbon–metal bond has two components. The first part comprises of a bond of σ character formed through the overlap between a metal hybrid orbital and the bonding π orbital (π_u) of acetylene, and is assumed to be largely responsible for the bonding. As the π_u orbital is doubly occupied in the free molecule, the formation of this σ bond necessarily leads to transfer of electron density from the acetylene onto the metal. It is assumed that this transfer of charge will be offset by the formation of a π-type bond through the overlap between a filled d_π orbital of the metal and an empty antibonding π orbital (π_g) of acetylene. The net effect of this bonding on acetylene is thus the removal of electron density from the π_u orbital, and a compensating buildup of charge in the π_g orbital.

Although this theory has gained wide acceptance, it has proved very difficult to find any evidence which unambiguously points to the formation of these π bonds. Attempts have been made to remedy this situation by measuring physical constants of the complexed acetylene and then comparing the results with the free-molecule values. For example, a study of the C≡C stretching frequency in a number of acetylene complexes revealed that, in many instances, it is decreased to a value more appropriate for a double, rather than triple, bond.[2,3] This may be interpreted as the result of π bonding, because the addition of electron density to the π_g orbital will reduce the C–C bond order which in turn would, presumably, reduce the vibration frequency. Results of this type are not, however, very conclusive.

Another interesting feature of the acetylene complexes is the change in the acetylene geometry which accompanies their formation.[4,5] Acetylene, which is linear in the free state, usually assumes a *cis*-bent structure in the complex. This change in geometry has been interpreted[6,7] as evidence of metal–carbon π bonding. because such a process would be expected to lead to an electron distribution analogous to that of the ^1A_u excited state of acetylene, which is known to be bent.[8] While being intuitively very attractive, this theory immediately presents two problems which must be resolved before it can be accepted. The first problem is that the analogy with the electron configuration of the

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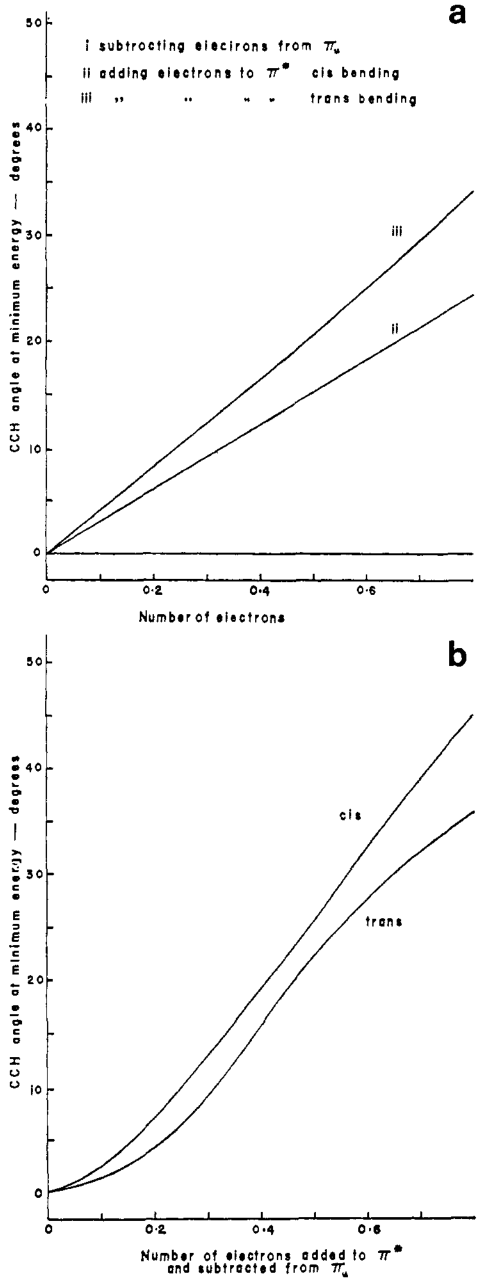

Figure 1. Variation of equilibrium CCH angle in acetylene with change in electron distribution: (a) separate addition of electron density to the π^* orbital and subtraction of density from the π_u orbital; (b) simultaneous addition to π^* and subtraction of an equal density from π_u.

^1A_u excited state is not complete, as may be seen as follows. If the *z* axis is taken to lie along the molecular axis, then the ground-state π-electron configuration is $(\pi_u{}^x)^2(\pi_u{}^y)^2$ ($D_{\infty h}$), where $\pi_u{}^x$ is the π_u orbital in the *zx* plane. The excitation of a π electron into an antibonding π orbital leads to a number of excited states, $^1\Sigma_u{}^-$, $^1\Sigma_u{}^+$, and $^1\Delta_u$, together with the corresponding triplet states. The ^1A_u state probably correlates with the $\Sigma_u{}^-$ state of the linear molecule,[9,10] which is derived from the electron configuration $(\pi_u{}^x)^1(\pi_u{}^y)^2(\pi_g{}^y)^1$ ($D_{\infty h}$), which, in the bent structure, becomes $(a_u)^1(b_u)^2(a_g)^1$ (C_{2h}). Turning now to the complexed acetylene, if the metal is taken to lie in the *xz* plane, the combined σ and π bonding may be expected to lead to an electron distribution in which the electron density is added to a π_g orbital in the same plane as the π_u orbital from which density was removed. This distribution would be of the type $(\pi_u{}^x)^1(\pi_u{}^y)^2(\pi_g{}^x)^1$ ($D_{\infty h}$) which corresponds more closely to the $^1\Delta_u$ or $^1\Sigma_u{}^+$, rather than to the $^1\Sigma_u{}^-$, excited state. Even here, the analogy is not complete, because the excited states have open-shell electron configurations, with the appropriate coupling of the electron spins. The second problem is that the observed excited-state geometry is *trans* bent,[8] whereas the complexed acetylene is always *cis* bent.

Although some theoretical evidence exists for a *cis*-bent excited state of acetylene,[9] the necessity of explaining why the *trans*-bent geometry is suppressed in favor of the *cis*-bent structure remains a barrier to the general acceptance of this theory. In the present paper, this problem is investigated theoretically, by using CNDO (complete neglect of differential overlap) molecular orbital theory[10,11] to calculate the bond angles of acetylene as a function of the electron densities in the π_u and π_g orbitals. The CNDO method lends itself particularly well to this purpose because, while being computationally very simple, it has proved very successful in the calculation of bond angles for a large range of molecules, in both their ground and lowest excited states. Significantly, the lowest singlet excited state of acetylene has already been successfully treated using CNDO theory.[9,12]

Theory

The model calculation discussed above can be performed by making a slight modification to the conventional CNDO method.[11,13] In particular, the bond-order matrix must be adapted to the acetylene electron distribution which results from the formation of the metal–acetylene bond.

Let the electron density which is removed from π_u through the formation of the σ part of the bond be ρ_π, and the electron density which is donated to the π_g orbital through π bonding be $\rho_\pi{}^*$. The bond-order matrix for the complexed acetylene is then given by

$$P_{\mu\nu} = 2\sum_i^{\text{occ}} C_{\mu i}C_{\nu i} + \rho_\pi{}^* C_{\mu l}C_{\nu l} - \rho_\pi C_{\mu k}C_{\nu k} \qquad (1)$$

where $C_{\mu i}$ is the coefficient for the μth atomic orbital in the *i*th (occupied) molecular orbital of acetylene. The letters *k* and *l* label the π_u and π_g orbitals, respectively.

The charge densities ρ_π and $\rho_\pi{}^*$ can be interpreted in terms of molecular orbital theory as follows. If the coefficient of π_u in the molecular orbital for a metal–acetylene σ bond is *g*, and the coefficient of π_g in the corresponding π orbital is *f*, then

$$\rho_\pi = 2 - 2g^2 \qquad (2)$$

$$\rho_\pi{}^* = 2f^2 \qquad (3)$$

Given the densities ρ_π and $\rho_\pi{}^*$, an approximate Fock matrix may be calculated for the complexed acetylene using eq 1 for the bond-order matrix, and the molecular energy and electron distribution can then be calculated using the conventional SCF procedure.[14]

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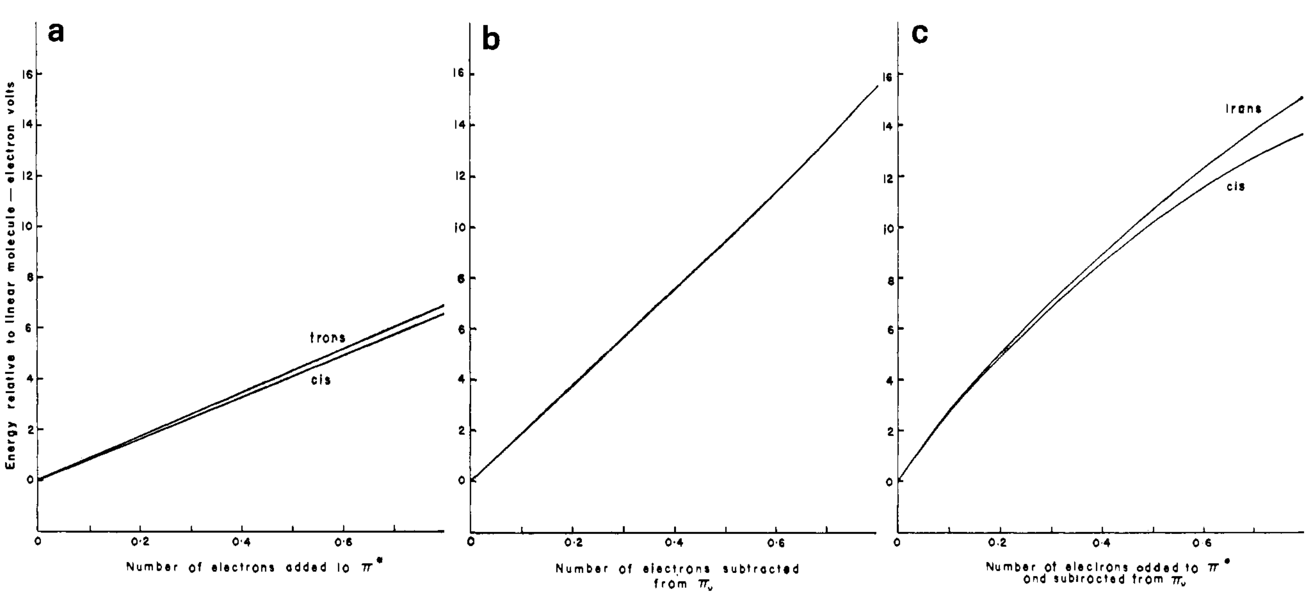

Figure 2. Variation of acetylene energy with change in electron distribution. The energy plotted here is the difference between that for linear acetylene with its normal electron distribution and that for acetylene bent at the equilibrium CCH angle for the specified electron distribution: (a) addition of electron density to the π^* orbital; (b) subtraction of density from π_u; (c) simultaneous addition to π^* and subtraction of an equal density from π_u.

In the present treatment a series of values is assigned to ρ_π and $\rho_\pi{}^*$ to represent the various degrees of σ and π bonding, and the molecular energy is then calculated as described above. The theoretical geometry of the complexed acetylene is calculated, for each pair of values for ρ_π and $\rho_\pi{}^*$, by minimizing this energy with respect to both *cis* and *trans* bending.

Theoretical Results for Acetylene

In the following section the geometry of acetylene is discussed in terms of the electron densities in the π_u and π_g orbitals and the effect of the metal–acetylene interactions.

As a range of C–C bond lengths are observed for acetylene in the various complexes,[4,5] it would appear necessary to repeat our calculations for several different values of this parameter. However, calculations based on both the free molecule bond lengths,[15] and the C–C bond length observed in $[(t\text{-BuC}{\equiv}\text{CBu-}t)(p\text{-toluidine})\text{PtCl}_2]^-$,[5] showed that bond-length changes of the magnitude observed have an insignificant effect on the final results. Hence all calculations presented here were performed using a single set of bond lengths (r_{CC} = 1.27 Å[5] and r_{CH} = 1.058 Å).

(a) Bond Angles. Figure 1a shows the geometry changes which result from the addition of electron density to the π_g orbital, or the subtraction of density from the π_u. It can be seen that the latter process does not lead to any change in geometry, the only effect being a steady increase in energy (Figure 2b). However, Figure 1a shows that if electron density is added to π_g, the linear molecule becomes unstable with respect to both *cis* and *trans* bending. Furthermore, the degree of bending induced is almost linearly proportional to the added electron density, with *trans* bending being slightly greater than *cis*. Figure 1b shows the effect of simultaneously adding and subtracting equal charge densities to and from the π_g and π_u orbitals, respectively. Qualitatively, the results are similar to those shown in Figure 1a; however, the simultaneous removal of electron density from the π_u orbital has enhanced both *trans* and *cis* bending.

So far, the calculations have shown that the electron distribution which is likely to result from π bonding can lead to either a *cis*- or a *trans*-bent acetylene. However, as yet it is not clear why the *cis* geometry is observed but not the *trans*. The possibility of a nonplanar geometry was also investigated, but the molecule was found to be planar for all the above electron distributions.

(b) Energies. The removal of electron density from the π_u orbital and its effective substitution in the π_g orbital will lead to a significant increase in the energy of acetylene. If the complex is to be stable this must, of course, be more than offset by the decrease in energy which results from the formation of the metal–acetylene bond. Unfortunately, we are only in a position to study the energy changes in the acetylene fragment. This is, however, of some interest, and probably has a bearing on the reason why the *trans* geometry is not observed.

The results of the energy calculations, for three electron distributions, are shown in Figure 2. The most significant feature of these diagrams is that they show that, for a given electron distribution, the *cis*-bent structure is lower in energy than the *trans*, by an amount which can be more than 1 eV. Although too much significance should not be attached to this result, it does offer some explanation for the absence of *trans*-bent complexes.

(c) The Metal–Acetylene Interaction. The calculations reported above are based on the assumption that the geometry of complexed acetylene is largely determined by forces from within the acetylene molecule itself. As this will only be true if the metal–acetylene bond is not weakened by the geometry changes considered, it is clearly necessary to discuss the dependence of the metal–acetylene interaction on the *cis*- and *trans*-bending coordinates.

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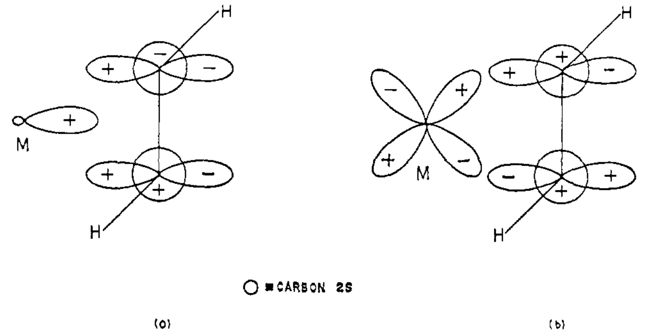

Figure 3. The relative signs of the 2s and $2p_\pi$ atomic orbital components of the π- and σ-bonding molecular orbitals for *trans*-bent acetylene: (a) π_u orbital with metal σ orbital; (b) π^* orbital with metal d_π orbital.

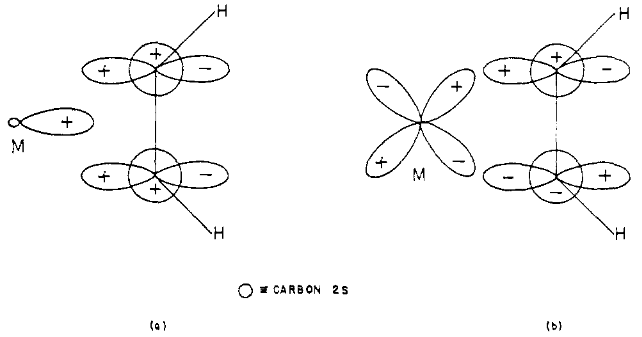

Figure 4. The relative signs of the 2s and $2p_\pi$ atomic orbital components of the π- and σ-bonding molecular orbitals for *cis*-bent acetylene: (a) π_u orbital with metal σ orbital; (b) π^* orbital with metal d_π orbital.

Both *cis* and *trans* bending of acetylene cause certain of the σ and π orbitals to mix through a reduction in the molecular symmetry. This mixing leads to a change in the composition of the π_u and π_g molecular orbitals, which in turn modifies their overlap with the central metal atom. The resultant dependence of the metal–acetylene overlap on the bending coordinates gives rise to a bending force, both directly through changes in the total energy of the complex, and indirectly through induced changes in ρ_π and ρ_π^*. Fortunately, many important properties of this force may be determined from symmetry arguments alone, without recourse to detailed calculations.

Although the original proponents of the current description of the metal–acetylene bond formulated their theory in terms of the π_u and π_g orbitals, there are no symmetry restrictions on the σ_g and σ_u orbitals also forming the same type of bonds. Thus the σ part of the metal–acetylene bond could be formed through the overlap between a filled σ_g orbital and a metal hybrid orbital, and the π bond could be formed through the overlap between an empty σ_u orbital and a metal d_π orbital. There is, however, an important distinction between the σ and π orbitals, in that the parities of the σ and π orbitals which occur in a given type of bond are reversed; σ_g goes with π_u, and σ_u with π_g. It follows from this discussion that a decrease in the overlap between the metal and the acetylene π orbitals will result if the symmetry of the bending coordinate is such as to allow σ and π orbitals of the same parity to mix. The resultant decrease in overlap will weaken the metal–acetylene bond and hence give rise to a strong force opposed to the bending.

Applying these arguments to the case of *trans*-bent acetylene, we see that as the *trans*-bending coordinate preserves a center of symmetry ($D_{\infty h} \rightarrow C_{2h}$), it only mixes σ and π orbitals which are of the same parity, as shown in Figure 3. Hence the *trans* bending of an acetylene molecule within a complex leads to a strong opposing force, which is derived from the weakening of the metal–acetylene bond. Furthermore, as *trans* bending must also lead to a reduction in ρ_π and ρ_π^* under these circumstances, this opposing force will be stronger than the intramolecular *trans*-bending force previously discussed, and the dominant force operating within the complex will therefore be opposed to the *trans* bending of the acetylene. Thus, according to the present theory, the absence of *trans*-bent acetylene complexes can be explained in terms of the weakening of the metal–acetylene bond which accompanies *trans* bending.

Turning to the *cis*-bent geometry, we find that the symmetry properties are now reversed. As the *cis*-bending coordinate preserves a plane of symmetry which connects the two hydrogens ($D_{\infty h} \rightarrow C_{2v}$), it mixes only σ and π orbitals which are of opposite parity, as shown in Figure 4. Thus the σ contributions, to both π orbitals in the *cis*-bent acetylene, are of the correct symmetry to overlap with the appropriate metal orbitals and to form the metal–acetylene bond. These σ overlaps will weaken or reinforce this bond depending on whether or not they are of the same sign as the corresponding π overlaps. The relative signs of the coefficients of the 2s and $2p_\pi$ orbitals, as found by calculation, are shown for both π molecular orbitals in Figure 4. The contributions from other σ atomic orbitals are not included in this diagram as they were found to be much smaller than that of the 2s orbital. It can be seen from Figure 4 that if the metal atom and the protons are situated on opposite sides of the C–C bond, all atomic overlaps will have the same sign and will combine to yield a large net overlap. However, if the metal and protons are on the same side of the C–C bond, the atomic overlaps will have opposite signs and will yield a small net overlap. Thus the theory predicts that there will be a strong force opposed to the *cis* bending of the protons *toward* the central metal. It is difficult to determine the magnitude or direction of the corresponding force for *cis* bending away from the metal, as this depends on the magnitudes of the $2s\text{–}d_\pi$ overlap as compared with the $2p_\pi\text{–}d_\pi$ overlap. In the case of Pt at least, a direct calculation shows these overlaps to be comparable in magnitude, $2s\text{–}5d_\pi = 0.232$ and $2p_\pi\text{–}5d_\pi = 0.189$,[16] so that *cis* bending away from the metal should have little effect on the strength of the metal–acetylene bond, and this contribution to the bending force may be safely neglected.

The discussion of the metal–acetylene interaction, which has just been outlined, raises the interesting question of the nature of acetylene orbitals which are responsible for the metal–acetylene bonding in the *cis*-bent complex. The present calculations suggest, in agreement with the accepted theory, that it is the π_u orbital which participates in the formation of the σ component of the bond. However, at experimental values of the *cis*-bending angle, this orbital does have a small, yet

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(16) These figures are based on the geometry given in ref 4.

nevertheless significant, contribution from a σ_g orbital. In the case of the π component, our calculations suggest that the situation is not as clear-cut, and that, in fact, the σ_u and π_g orbitals make about equal contribution to the metal–acetylene π bond. The calculations also suggest that the π-bonding orbital correlates with σ_u in the linear molecule.

In view of the strong mixing between the σ_u and π_g orbitals, the symbol π^* will be adopted for the π-bonding orbital in preference to π_g.

Comparison of Theoretical and Experimental Bond Angles

As the present theory is based on two empirical parameters, ρ_π and $\rho_\pi{}^*$, it does not lend itself to the prediction of the acetylene bond angles to be expected in a given complex. Also, the electron distribution cannot be determined unambiguously from the experimental geometry, as it is defined approximately by *two* parameters, ρ_π and $\rho_\pi{}^*$. However, Figure 1 does give some indication of the magnitude of the intramolecular bending force, so that a comparison with experimental data should show whether the proposed charge redistributions are physically reasonable.

The molecular geometries of the acetylenes in [(*t*-BuC≡CBu-*t*)(*p*-toluidine)PtCl$_2$]$^-$ [5] and [(triphenylphosphine)(diphenylacetylene)Pt][4] have been determined from the X-ray analysis of their crystal structures. The *t*-butylacetylene was found to be 15° *cis* bent while the diphenylacetylene was found to be 40° *cis* bent.

Turning to Figure 1, the first fact to emerge is that, according to the present theory, the presence of a *cis*-bent structure must indicate metal–carbon π bonding in the complex. This may be deduced from the fact that the removal of electron density from the π_u orbital does not by itself lead to a change in geometry. It can also be seen from Figure 1 that, if we limit ourselves to the simple electron distributions investigated in the present paper, the above bond angles can be accounted for by an effective transfer of respectively 0.35 and 0.7 electron from the π_u to the π^* orbitals. As no attempt has been made to find the electron distribution which optimizes the bending, it seems probable that the above densities represent an overestimate of the amount of charge which it is necessary to transfer in order to achieve the desired bond angles. The fact remains, however, that significant electron redistributions are necessary to achieve the observed bond angles. Although these electron transfers are rather larger than generally envisaged, it is observed experimentally that the excitation of one electron from π_u to π_g in acetylene leads to only a 60° (*trans*) bend.[8]

The *cis*-Bending Force. The origin of the *cis*-bending force in a complexed acetylene molecule can be determined from the variation of the atomic charge densities with this bending coordinate.

Let us consider the redistribution of electron density among the acetylene atomic orbitals which results from the formation of the metal–acetylene bond, which we simulate by the transfer of 0.3 unit of electron density from the π_u to the π^* orbital, and the corresponding electron redistribution which results from an increase in the *cis*-bending angle. These atomic charge redistributions, as represented by the differences in the atomic charge densities ($P_{\mu\mu}$), are set out in Tables I and II. A comparison of the density differences in these two tables shows that the electron redistribution which is produced by the change in geometry is exactly opposite to that produced by the formation of the metal–acetylene bond. It appears, therefore, that the acetylene intramolecular *cis*-bending force derives from the tendency of acetylene to reverse the atomic redistribution of electron density which is produced by the formation of the metal–acetylene bond and to approach the free-molecule electron distribution by mixing the σ_u and π_g molecular orbitals.

Table I. Difference between the Diagonal Elements of the Bond-Order Matrices for Acetylene with 0.3 Electron Removed from the π_u Orbital and Placed in the π^* Orbital, and Acetylene in the Usual Ground-State Electron Configuration[a]

Atomic orbital	h	2s	$2p_x$	$2p_y$	$2p_z$
Charge density	0.043	0.082	−0.134	0.0	0.010

[a] h = hydrogen 1s orbital, etc.

Table II. Difference between Diagonal Element Matrices for 4° *cis*-Bent Acetylene, and 1° *cis*-Bent Acetylene[a]

Atomic orbital	h	2s	$2p_x$	$2p_y$	$2p_z$
Charge density	−0.009	−0.016	0.028	0.0	−0.003

[a] The electron distribution in both cases corresponds to 0.3 electron added to π^* and 0.3 electron removed from π_u.

The above discussion suggests that there are two, almost complementary, bending mechanisms for acetylene. According to Walsh,[17] the *trans*-bending force derives from the mixing of σ_g character into the π_g orbital, whereas we have found that, in the case of *cis* bending, the force derives from the mixing of π_g character into a σ_u orbital.

Summary and Conclusions

The nature of the bonding between acetylene and a central metal atom, in a transition metal complex, has been investigated using an idealized model which mainly considers the interactions within an isolated acetylene molecule. It was hoped that this investigation would help to determine whether or not the presence of a *cis*-bent acetylene in a complex indicated π bonding of the type described in the introduction, and also add to the qualitative description of the π bond.

The calculations showed that the addition of electron density to the π^* orbital could lead to either a *cis*- or a *trans*-bent acetylene structure, with the *cis* structure being slightly lower in energy. The removal of electron density from the π_u orbital did not lead to a change in geometry by itself, but when it accompanied the addition of density to π^* it strongly enhanced the bending. It was also shown, using symmetry arguments, that the *trans* bending of a complexed acetylene led to a weakening of the metal–acetylene bond, and that the dominant force within the complex is therefore opposed to this change in geometry. The same argument suggested that *cis* bending of protons of the complexed acetylene away from the central metal probably has little effect on the strength of the metal–acetylene bond, so that the acetylene geometry is largely determined by the *cis*-bending force calculated in the previous sections.

These results suggest that, according to the present theory, the presence of *cis*-bent acetylene in transition metal complexes is a strong indication of π bonding.

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Furthermore, they help to clear up some of the paradoxes of the excited-state theory discussed in the introduction, and to clarify the relationship between π bonding and the $\pi^* \leftarrow \pi$ excited states.

Turning now to the nature of the acetylene orbital which is used to form the metal–acetylene π bond, we find that at experimental values of the *cis*-bending angle it is an almost equal mixture of π_g and σ_u molecular orbitals. As the σ_u orbital is antibonding between the carbon 2s orbitals, the formation of the metal–acetylene π bond will lead to a reduction in the 2s character of the acetylene carbon–carbon bond, which should be reflected by a corresponding reduction in the carbon–carbon nuclear spin coupling constant.

The above discussion suggests that the theory of metal–acetylene π bonding could be tested experimentally by measuring the change in the acetylene C≡C nuclear spin coupling constant which accompanies the formation of an acetylene complex.

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The Hydrogen-Bonding Interaction of Aromatic Amine Oxides with Phenols

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Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received April 5, 1968*

Abstract: The use of pyridine 1-oxide σ constants (σ_{pyNO}) has been extended to the quinoline 1-oxide system. The hydrogen-bonding interactions of *p*-chlorophenol, phenol, and *p*-methylphenol with 4-substituted pyridine 1-oxides and 4- and 6-substituted quinoline 1-oxides (the substituents being $(CH_3)_2N$, CH_3O, CH_3, H, Cl, Br, CN, CO_2CH_3, and NO_2) have been studied. ΔH values for the reactions have been calculated and are tabulated. Correlations have been obtained with σ_{pyNO} constants for the change in the hydrogen–oxygen stretching frequency $\Delta\nu_{\mathrm{OH}}$. It is found that $\Delta\nu_{\mathrm{OH}}$ frequencies for the interactions with 4-substituted pyridine 1-oxides and 4-substituted quinoline 1-oxides correlate with σ_{pyNO} constants, whereas, the $\Delta\nu_{\mathrm{OH}}$ values for the interactions of 6-substituted quinoline 1-oxides are best correlated with Hammett σ constants.

The availability of several 4-substituted pyridine 1-oxides[3] has prompted many attempts to correlate substituent constants for the various groups with observable properties of either the N-oxides themselves or their complexes. In almost every instance it was necessary to use adjusted Hammett σ constants (σ^+, σ^-, or σ^*) rather than the σ constants themselves in order to obtain these correlations. In fact, some correlations utilized σ^+, σ, and σ^- on the same plot.

Many reasonable correlations between measured physical properties of a system containing substituted pyridine 1-oxides and a hybrid set of substituent parameters have been found.[4-14] Nevertheless, it is indeed unfortunate that one single set of substituent parameters has not been employed. As is now the practice, use of a hybrid set of substituent parameters makes comparison of the various properties of analogous systems very difficult. Anomalies of interaction are not easily recognized.

Therefore, we suggested a return to the fundamental definition of substituent parameters. An internally self-consistent set of values based upon the measured acid dissociation constants, K_{BH^+}, was calculated from the Hammett relationship[15] for the pyridine 1-oxides. All of the presently available data may be satisfactorily correlated with σ_{pyNO} constants. There exists no example to our knowledge where adjusted σ_{pyNO} values are necessary.

Until now, no correlations have been made with any of the properties of the quinoline 1-oxides. An investigation of the hydrogen-bonding properties of a series of 4- and 6-substituted quinoline 1-oxides was undertaken to test the applicability of these new constants and to compare the properties of the quinoline 1-oxides with those of the pyridine 1-oxides. The hydrogen-bonding properties of the 4-substituted pyridine 1-oxides were also investigated[6] for comparison purposes. The hydrogen–oxygen stretching frequency, ν_{OH}, of phenols upon hydrogen-bond formation is sensitive to base strength.[16-19] *p*-Chlorophenol, phenol,

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