THE EFFECT OF METALLOID SUBSTITUTION ON THE ELECTRONIC SPECTRA OF SIMPLE CHROMOPHORES

ROBERT WEST
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)
(Received August 31st, 1964)

In this paper a qualitative molecular orbital method will be applied to predict the effect of metalloid substitution on electronic transitions of two- and three-atom chromophores. In recent years organometallic derivatives of several simple chromophores have been synthesized and electronic spectra for a limited number of such compounds have been reported[1-8]. Most of the compounds studied to date are organosilicon compounds, and of these the most widely discussed have been the α-silylcarbonyl compounds first described by Brook[1,2]. A silicon or germanium substituent attached to a carbonyl carbon has a pronounced bathochromic effect on the long wave-length ($n \rightarrow \pi^*$) carbonyl transition, and all known α-silyl ketones are visibly yellow. Recently an explanation for this bathochromic effect, based on qualitative application of molecular orbital theory, was proposed independently by Harnish and West[9] and by Orgel[10]. The present paper represents a generalization of this explanation to a variety of chromophores.

In its present extended form this method may be helpful both in rationalizing existing data and in predicting the spectral properties of organometalloid derivatives as yet unknown. So long as the method is restricted to simple two- and three-atom chromophores, it can be applied without extensive use of symmetry theory; all that is needed for predictions to be made is that the structure of the chromophore be known, and its transitions identified as to their nature.

In summarizing the effect of silicon substituents on electronic transitions, Eaborn[11] has stated that "bathochromic shifts are usually found." As will be seen, this statement should be true for the majority of simple chromophores, though not for all. On the other hand, it will be shown that ground-state pi-bonding, which has sometimes been proposed to account for spectral shifts upon silicon substitution[6,7], represents an incomplete and misleading explanation which would in many cases lead to effects opposite from those observed.

Some limitations on the generality of the method are now necessary. In its present highly qualitative form the theory is limited to prediction of the direction of spectral shifts for simple chromophores, and only the roughest estimates of magnitudes can be made. The discussion in this paper will be limited to two- and three- atom chromophores; extension to related cases may be possible, but complicated chromophoric systems such as substituted aromatic rings, etc., will not here be considered. The metalloid substituents to which the discussion will apply are those electropositive elements which form predominantly covalent bonds to the chromophores, and which have vacant orbitals into which they can accept electronic charge from lone pairs or from pi-orbitals on adjacent atoms by dative pi-bonding. It will further be assumed that dative pi-bonding will dominate over other effects in determining the energy of electronic transitions. For most of the chromophores to be discussed, we believe this to be a reasonable expectation for silicon and germanium, for tricoordinate boron, aluminum and gallium and for pentavalent arsenic and antimony. The extent to which other metallic elements can be expected to follow the rules given below will be discussed later.

The general method of approach follows that used previously to account for the influence of electronegative substituents on chromophores, as clearly explained by Jaffe and Orchin[12]. The systems which we will consider can be represented as M–A–B or M–A–B–C, where M is the metallic element and A–B or A–B–C is the chromophore, containing at least one normal pi-bond. For such systems, electronic absorption in the ultraviolet and visible region is associated with transitions from lone pairs to antibonding pi-orbitals of the chromophore ($n \rightarrow \pi^*$ transitions), or from bonding pi-orbitals to antibonding pi-orbitals ($\pi \rightarrow \pi^*$ transitions). We will now distinguish four cases for more detailed discussion.

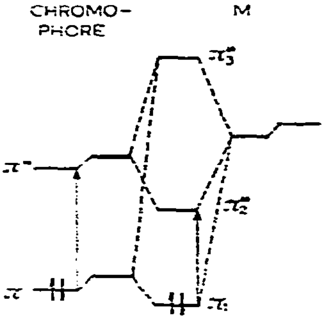

Fig. 1. Energy level diagram for a Class I chromophore showing the effect of metalloid substitution. Both the inductive and the resonance effect of the substituent are diagrammatically indicated.

Case I

Pi-bonding only with no lone pairs. Examples: M–C=C–, M–C≡C–. A bathochromic shift is predicted. The M.O. diagram for the levels in question is as shown in Fig. 1. Construction of the diagram begins with the orbitals of the separated olefin and metal atom. Both inductive and resonant interaction can take place with the metalloid substituent M. The inductive effect of the electropositive substituent is to raise both π and π^* by a small and indeterminate amount, while the vacant pi-type orbital of the metal will be lowered by a similar small amount. Resonant interaction will also take place between the vacant metal orbital and both π and π^*, to generate three new levels, which in the figure are designated π_1, π_2, and π_3. However, because of better energy matching, interaction of the metal orbital is expected to be substantially stronger with the π^* antibonding level than with π (Fig. 1).

The olefin electronic absorption must be only of the $\pi \rightarrow \pi^*$ type, in which an electron moves from the bonding to the antibonding pi-level[12]. π_1 and π_2 should be closer in energy than the corresponding levels π and π^* were in the original olefin, and so stabilization of the excited state is predicted, and a bathochromic (red) shift is predicted for the transition. However, because the bonding π level is also being lowered to some extent by resonant interaction with M, in certain cases the shift may not be large.

A crude calculation will suffice to show that the relative ordering of levels in Fig. 1 is reasonable. The ionization potential for ethylene is 10.45 eV[13], and the $\pi \rightarrow \pi^*$ transition energy is 62,000 cm^{-1} or 7.68 eV[14]. Subtracting these values, it is found that the π^* level lies 2.77 eV below the reference, which will be taken as complete ionization. The ionization potential for silicon, chosen as a typical metalloid, is 8.15 eV[15], and the $3p \rightarrow 3d$ promotional energy for the atom, averaged over various states, is 6.20 eV[15]. Subtracting once again, the energy of the $3d$ level for silicon is found to be 1.95 eV below reference, or about 0.8 eV above π^**.

The simple olefinic chromophore gives electronic absorption only in the vacuum ultraviolet region, but conjugation shifts the $\pi \rightarrow \pi^*$ absorption toward the visible. There is little information in the literature on the effect of metal substitution on polyene spectra. By extension, Case I also includes acetylenic compounds, though the detailed molecular orbital argument is much more complicated for triple bonds. In agreement with prediction, the compound $Et_3SiC{\equiv}C{-}CMe{=}CHMe$ shows a modest bathochromic shift of 2100 cm^{-1} compared to the unsubstituted compound[8]. Disilylacetylene also appears to show a bathochromic shift compared to 2-butyne**.

Case II

Pi-bonding at atom A, but lone pairs only on atoms B or C. Examples: $M{-}C{=}O$, $M{-}C{=}N{-}$, $M{-}C{=}S$, $M{-}NO_2$, $M{-}CO_2^-$. For the long wave length transition, a marked bathochromic shift is predicted. This case includes the now-classical example of the

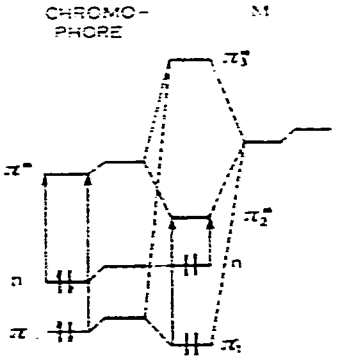

Fig. 2. Energy level diagram for the carbonyl group, a typical Class II chromophore, showing the effect of metalloid substitution.

---

* The position of the $3d$ level in silicon is calculated relative to the atomic ground state. The valence-state ionization potential and the $3p \rightarrow 3d$ promotional energy from the valence state might alternatively have been used, but it is felt that this procedure would give an even less realistic estimate of the relative energy of the $3d$ level, unless bonding terms were introduced into the calculation. Similar order-of-magnitude calculations have been carried out for other metalloids; the nonbonding pi-type orbital of the metal is always predicted to lie much closer to π^* than to π. The same is true if the chromophore is $C{=}O$ (*vide infra*).

** In these monoacetylenes, the band maximum lies below 2000 Å and was not determined, but absorption extends noticeably farther into the accessible ultraviolet region for the silicon compound[8a].

carbonyl group. A generalized M.O. diagram for Case II groups is shown in Fig. 2. In addition to the bonding and antibonding π-levels, there will be one (or more) nonbonding filled level(s) corresponding to the lone pair(s) on atom B, here designated n; and the electronic transition of lowest energy will be $n \rightarrow \pi^*$. M can interact inductively with levels π, n and π^*; but because n is located on the more remote atom B, significant resonance interaction can take place only with π and π^*. Furthermore, relative energies are such that there should be much greater resonant interaction with π^* than with π.

As shown in Fig. 2, the predicted effect of metalloid substitution is greatly to lower the energy of the $n \rightarrow \pi^*$ transition. The data published by Brook and his coworkers show that silicon or germanium substitution alpha to a carbonyl group leads to a shift the $n \rightarrow \pi^*$ transition of about 6000 cm^{-1} in the expected direction[2]. Another possible example consistent with the prediction is provided by the recently discovered, visibly colored carbonyl derivatives of decaborane[9].

The $\pi \rightarrow \pi^*$ transition for Class II groups, in those cases where it may be observable, should be affected by M in much the same way the olefin $\pi \rightarrow \pi^*$ transition and so a bathochromic shift is also predicted.

Case III

Three-atom systems with lone pair on atom A, but pi-bonds only between B and C. Examples: M–azide; M–O–C=O; M–N–C=O; M–O–C=C–, etc. A hypsochromic shift is predicted for those electronic transitions involving transfer of charge from the lone pair on atom A. The carboxylate ester group, recently studied by Closson and Haug[17], will be discussed as a typical example. Fig. 3 shows energy levels for the

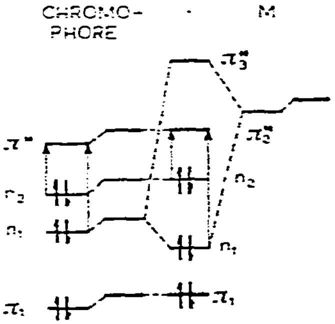

Fig. 3. Energy levels for the carboxylate ester group, a Class III chromophore, as influenced by metalloid substitution. The assignments follow those of Closson and Haug[17], but the notation used differs slightly.

ester group, as influenced by metal substitution at oxygen. Level n_2 is a non-bonding pair on the carboxyl oxygen, whereas n_1 is essentially a non-bonding pair on the ether oxygen. The unfilled orbital on the metal can interact only with n_1, and so will cause a small hypsochromic shift of the $n_1 \rightarrow \pi_2$ transition. The metal can influence the energy of the $n_2 \rightarrow \pi_2$ transition only indirectly, and so little change is predicted for this absorption, which is believed to be the one occurring at lowest energy in most esters. Many organometallic carboxylate esters have been prepared, but spectral data are lacking.

The azide chromophore, which also falls in this class, has been treated recently by Closson and Gray[18]. The effect of metal substitution has been discussed by Thayer and West in a paper on azidotrimethyl compounds of the Group IV elements, to which the reader is referred for a more complete treatment of this chromophore[4]. Briefly, the azide group can be considered as a triply-bonded nitrogen molecule attached to a nitrogen atom by sigma- (and some pi-) -bonding, *i.e.* $\mathrm{M{-}N\overset{...}{=}N{\equiv}N}$. The two transitions observed in the ultraviolet spectrum are both of $n \rightarrow \pi^*$ type, in which charge is transferred from lone pairs on the first nitrogen (atom A) to antibonding M.O.'s of the pi-systems. Metalloid substitution can only stabilize the ground state, and is predicted to cause a moderate hypsochromic shift in one of these transitions and little change in the other. This expectation is borne out by the observed spectrum of $\mathrm{Me_3SiN_3}$ and $\mathrm{Me_3GeN_3}$[4].

Case IV

Both lone pair and antibonding pi-orbitals on atom A. Examples: $\mathrm{M{-}N{=}N{-}}$, $\mathrm{M{-}N{=}C{-}}$, $\mathrm{M{-}N{=}O}$. A bathochromic shift of the $n \rightarrow \pi^*$ absorption is generally expected, but exceptions to this general rule are possible. The energy level diagram for Case IV will differ depending on whether the low-energy vacant orbital on the metal is of *p* or *d* type. A typical energy level diagram for a metalloid with vacant *d* orbitals is shown in Fig. 4*. The metalloid orbitals can now interact both with *n* and with π^*.

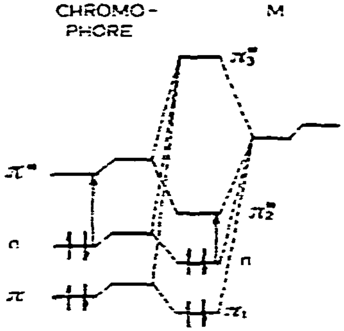

Fig. 4. Energy levels for a Class IV chromophore, showing the influence of a metalloid substituent with unfilled *d* orbitals. Only one nonbonding pair is indicated (*n*), as in $\mathrm{M{-}N{=}C{<}}$.

For most compounds, the energy match should be better with π^* than with *n*, so greater resonant interaction is expected with the antibonding pi-level. This should lead, as in Case II, to stabilization of the excited state and a marked bathochromic shift of the $n \rightarrow \pi^*$ band. Such a shift is found for silicon compounds of the type $\mathrm{R_3Si{-}N{=}N{-}Ph}$, which absorb near 5850 Å[9] in the visible region and so appear blue

---

* If the metalloid atom is one with only a vacant *p* orbital available, such as boron, interaction can take place either with π^* or with *n*, but not both at once. π^* and *n* are mutually orthogonal, and so a *p* orbital can overlap only with one of them. For such overlap to take place, it is also required that the *p* orbital be coplanar or nearly so with the interacting orbital. In molecules where there is no strong geometrical preference, one might expect the molecule to adopt a conformation favoring dative pi-bonding from *n* in the ground state, but in the electronic excited state to adopt a conformation rotated by 90° at the M-A bond, and so favorable for π^*-*p* interaction.

in color[5,6*]. The observed shift is about 6000 cm^{-1} from CH_3–N=N–Ph[19], or 5500 cm^{-1} from azobenzene[20].

In Case IV, it is possible that some molecules will be found in which interaction of the metal orbitals is greater with n-levels than with π^*. There must be strong ground-state dative pi-bonding in the linear molecules of silyl isocyanate[21] and isothiocyanate[22], for example. If the resonant interaction with n were greater than with π^* a hypsochromic shift would be predicted for the $n \rightarrow \pi^*$ transition. Additional examples of Case IV compounds will be of special interest in this connection.

DISCUSSION

A few generalizations can now be drawn from the four cases discussed above. When pi-bonding to a metal can take place from antibonding pi-orbitals, stabilization of the excited state will result, and transitions to the antibonding level will be shifted to lower energy. When pi-bonding can take place only from a lone pair on the atom bonded to the metal, the ground state will be stabilized, and transitions from the lone pair will be shifted to higher energy. Generally speaking, because of better energy matching of orbitals, excited-state pi-bonding should be more effective than ground-state pi-bonding; therefore bathochromic shifts caused by metal substitution will generally be larger than hypsochromic shifts.

For highly electropositive metals, pi-bonding is likely to be less important in determining the energy of electronic transitions, and simple inductive effects will be more important. There is little comparative data available, but the recent study of trimethyl azides of Group IVA elements is relevant[4]. The silicon and germanium compounds were found to follow the expectation for Case III above, but the tin and lead compounds did not show the predicted hypsochromic effects; instead, the inductive effect of the metals appeared to be the predominant factor influencing the electronic spectra. However, the relative importance of inductive *vs.* pi-bonding effects will doubtless differ for other chromophores, and so the point at which pi-bonding will cease to be the dominant factor may vary from one chromophore to another. The metals arsenic, antimony and bismuth in the trivalent state, and the transition metals generally, bear unshared electrons and so could interact with chromophores either as pi-donors or as pi-acceptors. An extension of the theory outlined here may possibly be useful in dealing with these metals, but at present very little data is available against which to check any predictions which might be made.

In order to evaluate the generality of the theory, comparative studies of organometallic derivatives of various simple chromophores are badly needed. Exceptions to the broad principles outlined here are to be expected, but it is believed that the rules set forth here can serve for the moment as a standard against which the spectral properties of metal compounds can be judged.

ACKNOWLEDGEMENTS

For helpful discussions, the author is indebted to Drs. R. F. FENSKE, A. SADŌ,

---

[*] Two $n \rightarrow \pi^*$ absorption bands are theoretically possible for azo compounds, but only one is normally observed. A bathochromic shift relative to the metal-free reference compound is also shown by Me_3Si–NPh_2[7], but band assignments have not been made.

and J. S. Thayer, and especially to D. F. Harnish, who was the first to use the approach outlined in this paper in special cases. This work was supported by a grant from the Air Force Office of Scientific Research of the Air Research and Development Command.

SUMMARY

Qualitative molecular orbital theory is applied to the prediction of the effect of metalloid substitution on the electronic spectra of simple two- and three-atom chromophores. This theory proceeds from the assumption that dative pi-bonding can take place from unshared pairs or from pi-type orbitals on adjacent atoms into unfilled orbitals on the metal, and that such pi-bonding will predominate over other effects in determining the energies of electronic transitions.

The predicted effect of metalloid substitution depends on the nature of the chromophore. For some chromophores (those in Case II above, including $>C=O$), the only interaction possible for the metal is that with antibonding pi-orbitals to stabilize the excited state, and a bathochromic shift of the principal electronic transition is predicted. For a few chromophores (Case III above) interaction is possible only with lone pairs to stabilize the ground state, and hypsochromic shifts are predicted upon metal substitution. Finally, there are many chromophores for which both types of interaction are possible (Cases I and IV above); either ground-state or excited-state stabilization is possible upon metalloid substitution, but energy considerations suggest that the latter will usually be favored, and that bathochromic shifts will be the general rule.

REFERENCES

1 A. G. Brook, *J. Am. Chem. Soc.*, 79 (1957) 4373.
2 A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz and C. M. Warner, *J. Am. Chem. Soc.*, 82 (1960) 5102.
3 J. S. Thayer and R. West, *Inorg. Chem.*, 3 (1964) 406.
4 J. S. Thayer and R. West, *Inorg. Chem.*, 3 (1964) 889.
5 U. Wannagat and C. Krüger, *Z. Anorg. Allgem. Chem.*, 326 (1964) 288, 304.
6 C. Krüger and U. Wannagat, *Z. Anorg. Allgem. Chem.*, 326 (1964) 296.
7 C. Krüger, E. G. Rochow and U. Wannagat, *Chem. Ber.*, 96 (1963) 2132.
8 K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, (1946) 948.
8a E. A. V. Ebsworth and S. G. Frankiss, *J. Chem. Soc.*, (1963) 661.
9 D. F. Harnish and R. West, *Inorg. Chem.*, 2 (1963) 1082.
10 L. E. Orgel, quoted in E. B. Ebsworth, *Volatile Silicon Compounds*, Pergamon Press, Oxford, 1963, p. 81.
11 C. Eaborn, *Organosilicon Compounds*, Butterworth, London, 1960, p. 484.
12 H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962, pp. 175–182.
13 F. H. Field and J. L. Franklin, *Electron Impact Phenomena*, Academic Press, New York, 1947, p. 253.
14 J. R. Platt, H B. Klevens and W. C. Price, *J. Chem. Phys.*, 17 (1949) 466.
15 *Atomic Energy Levels*, Vol. I, National Bureau of Standards Circular No. 467, Washington, D.C., 1949, pp. 144–146.
16 W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler and E. L. Muetterties, *J. Am. Chem. Soc.*, 86 (1964) 3973.
17 W. D. Closson and P. Haug, *J. Am. Chem. Soc.*, 86 (1964) 2384.
18 W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, 85 (1963) 290.
19 M. P. Grammaticakis, *Bull. Soc. Chim. France*, (1947) 438.
20 A. Burawoy, *J. Chem. Soc.*, (1937) 1865.
21 F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 17 (1961) 977.
22 D. R. Jenkins, R. Kewley and T. M. Sugden, *Proc. Chem. Soc.*, (1960) 220.