ment of toluene, reported variously to be 0.3 to 0.5 D.,[23] with 0.4 D. being generally accepted as the best value.

The fact that the moment of the unsymmetrical hydrocarbon (I) is slightly greater than that of ethanoanthracene (VIII) can be perhaps explained by the strained methano bridge in the former compound. That such strain can give rise to electrical dissymmetry

(23) L. G. Wesson, "Tables of Electric Dipole Moments," Massachusetts Institute of Technology Press, Cambridge, Mass., 1948, p. 36.

is suggested by the surprisingly large dipole moment (0.58 D.) reported by Krieger[24] for norbornane.

(24) H. Krieger, *Suomen Kemi.*, **31B**, 348 (1958).

---

# Physical and Theoretical Studies on Some Solid Complex Diazonium Salts of p-Dimethylaminobenzenediazonium Chloride. II. Spectral Studies

By Edward A. Boudreaux,[1] Hans B. Jonassen, and Leroy J. Theriot

The qualitative aspects of charge-transfer spectra anticipated in complexes of p-dimethylaminobenzenediazonium chloride with various anhydrous metal chlorides have been calculated using a semiempirical procedure. In this model it is proposed that a nonspecific charge transfer from the diazonium donor to the metal chloro species (acceptor) is involved. The calculated results are found, within the inherent limitations and approximations of the procedure, to be in general agreement with the observed reflectance spectra of the solid compounds.

## Introduction

In part I of this publication series the magnetic properties of p-dimethylaminobenzenediazonium chloride complexed with a variety of metal chlorides were determined. The results were interpreted to be indicative of what is expected if a charge-transfer interaction were involved. In this part of the study the spectra of the solid compounds measured in the visible and ultraviolet regions are accounted for qualitatively on the basis of a semiempirical theoretical treatment. Again the results seem to support the existence of charge-transfer phenomena as indicative of the interaction between the organic and inorganic components in these compounds. To the authors' knowledge, this is the first time spectral measurements on solid compounds of this type have been reported, and any sort of theoretical account given of the observed spectra.

## Experimental

**Preparation and Analysis.**—The preparation and chemical analyses characterizing these compounds have already been described in detail in part I. The empirical formulas for the compounds of interest are[2]: $(Dz)FeCl_4$, $(Dz)_2MnCl_4$, $(Dz)_2CoCl_4$, $(Dz)CuCl_3$, $(Dz)_2ZnCl_4$, $(Dz)CdCl_3$, $(Dz)SbCl_6$, $(Dz)BiCl_4$, $(Dz)_2SnCl_6$, and $(Dz)_2TeCl_6$.

**Solution Spectra.**—The spectra of the compounds were determined in anhydrous ethanolic solutions having solute concentrations of about $10^{-4}$ M. A Beckman model DB automatic recording spectrophotometer equipped with quartz absorption cells was employed.

**Solid State Spectra.**—The spectra of the solid compounds were determined by the usual reflectance techniques with a Beckman model DU spectrophotometer equipped with a reflectance attachment. Reflectance measurements were made relative to an $MgCO_3$ standard for the visible and high purity polished aluminum for the ultraviolet. The results were converted to absolute reflectance by correcting for the known reflectance of the standards in the visible and ultraviolet regions.[3]

**Method of Calculation.**—In the present treatment the primary charge-transfer process involves the transfer of an electron from the diazonium component (donor) to the metal chloro species (acceptor). In this respect the interaction is analogous to that typical of ionic salts such as sodium chloride, in which the charge transfer involves the transfer of an electron from sodium to chlorine. This may be expressed quantum mechanically as

$$\psi_N(D,A) = a\psi_0(D,A) + b\psi_1(D^+A^-)$$

where $\psi_N$ is the complete wave function for the ground state of the complex, $\psi_0$ the "no bond" function, and $\psi_1$ the dative bond function representing a complete electron transfer from the donor D to the acceptor A. It is also assumed that in the excited state the electron transfer is still from the donor to the acceptor, since the acceptor in this case is a stable complex anion (*i.e.*, a separate entity with tightly bound closed electron shells), whereas the donor is an aromatic cation in which the highest energy-filled orbital should be rather diffuse. Consequently it would seem that the optically-induced electron transfer would be somewhat energetically more favorable from the donor to the acceptor.

Application of the variational principle and perturbation theory to the above equation leads to the result[4]

$$(h\nu)_{CT} = (W_1 - W_0)\left[1 + \left(\frac{H_{01} - W_1 S_{DA}}{W_1 - W_0}\right)^2 + \left(\frac{H_{01} - W_0 S_{DA}}{W_1 - W_0}\right)^2\right] \quad (1)$$

where $(h\nu)_{CT}$ is the energy of the charge-transfer process, and $S_{DA}$ is the donor–acceptor overlap, defined as $\int \phi_0 \phi_A d\tau$, $\phi_D$ being the highest energy filled orbital of the donor and $\phi_A$ the lowest energy unfilled orbital of the acceptor. The other terms have their usual significance. It is further known that[5] in eq. 1, $(W_1 - W_0) = \Delta W(I_D - E_A - e^2/r_{DA} + \beta)$, where $I_D$ is the ionziation potential of the donor, $E_A$ the electron affinity of the acceptor, $r_{DA}$ the equilibrium donor–acceptor separation, and $\beta$ the resonance integral. Thus $\Delta W$ may be either positive or negative depending upon whether $W$ or $W_0$ is larger. For the diazonium salt complexes, both donor and acceptor must be charged in order for the complex to be stable; hence $W_0 < W_1$ so that $\Delta W$ is negative. The variation method also gives the result, $-b/a = (H_{01} - S_{DA}W_0)/(W_1 - W_0)$, with a similar expression for the excited state function. However, $b/a = (\Delta_{ic}/1 - \Delta_{ic})^{1/2}$, where $\Delta_{ic}$ is the fractional ionic character, is an equally valid relationship in the valence bond treatment. Finally, substitution of these relationships into 1 and rearranging gives

$$(h\nu)_{CT} = [1 + 2(\Delta_{ic}/1 - \Delta_{ic}) + 2(\Delta_{ic}/1 - \Delta_{ic})^{1/2} S_{DA} + S_{DA}^2](\Delta W) \quad (2)$$

It is evident from 2 that the calculation of $(h\nu)_{CT}$ requires the determination of $I_D$, $E_A$, $\Delta_{ic}$, $S_{DA}$, $r_{DA}$, and $\beta$, in which $I_D$ and $E_A$ are the most important quantities involved. Unfortunately, experimental values of these latter two quantities are not known for the complex cases involved here, and any rigorous theoretical calculations leading to them are out of the question. Hence one is forced to be content with reasonable estimates of their values.

**Evaluation of $I_D$.**—The ionization potential of the p-dimethylaminobenzenediazonium donor was estimated by comparing the relative trends in ionization potentials of p-disubstituted benzenes given in the literature.[6a,b] The gas phase ionization potential was

(1) Extracted in part from the Ph.D. Dissertation of Edward A. Boudreaux, to whom requests for reprints should be sent at the Louisiana State University in New Orleans, New Orleans, La.

(2) The symbol Dz represents the p-dimethylaminobenzenediazonium ion.

(3) (a) F. Benford, G. P. Lloyd, and S. Schwarz, *J. Opt. Soc. Am.*, **38**, 445 (1948); (b) F. Benford, *et al.*, *ibid.*, **38**, 964 (1948).

(4) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

(5) S. H. Hastings, J. L. Franklin, J. C. Schiller, and F. A. Matsen, *J. Am. Chem. Soc.*, **75**, 2900 (1953).

(6) (a) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); (b) K. Watanabe and J. R. Mottle, *ibid.*, **26**, 1773 (1957).
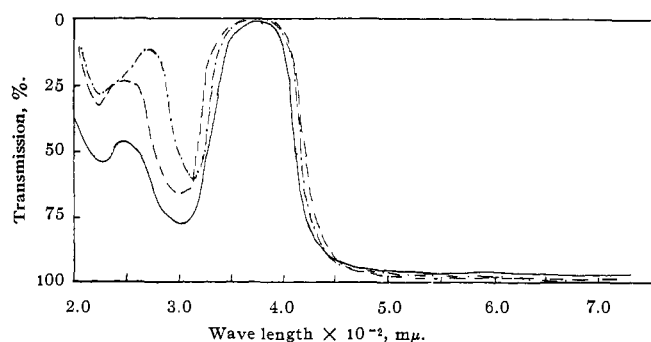
Fig. 1.—Some typical ultraviolet–visible solution spectra of diazonium salt complexes. The solutions of absolute ethanol are about $\times 10^{-4}$ $M$ in solute concentrations. The differences in the intensities of the maxima are due to the inability to control solute concentrations to any high degree of accuracy: ———, DzCl; – – – –, $(Dz)_2MnCl_4$; $\cdot—\cdot—\cdot—$, $(Dz)SbCl_6$.

estimated from the ionization potential of dimethylaniline[7] adjusted for the electronic effects of the *p*-substituted diazonium group in accord with considerations previously investigated.[8] The resulting value (7.9 e.v.) was then reduced to a reasonable value for the solid by applying the principles of Lyons[9] and Kearns and Calvin.[10] The result is an $I_D$ of 7 e.v. with an average deviation of about ±0.3 e.v. It is quite possible that this result may be in error by 0.3–0.5 e.v.; hence the difference between the ionization potentials for the gaseous and solid states may be significantly less than 0.9 e.v. since polarization by a dipole is actually involved rather than single charges.

TABLE I
ESTIMATED ELECTRON AFFINITIES OF METAL ATOMS

| Atom | (mS.R.)[a] | $E_A$, e.v. (lit.)[b] | $E_A$, e.v. (interpol.)[c] |
|------|-----------|------------------------|----------------------------|
| Fe | 5.86 | ... | 1.2 |
| Mn | 5.17 | ... | −0.6 |
| Co | 5.46 | ... | 0.2 |
| Zn | 4.93 | −1.2 | −1.2 |
| Cd | 5.04 | −1.1 | −0.9 |
| Hg | 4.95 | 0.8 (?) | −1.2 |
| Sb | 5.98 | 1.3 | 1.5 |
| Sn | 5.87 | 1.2 | 1.3 |
| Te | 6.41 | 2.1 | 2.1 |
| Bi | 5.84 | ... | 1.2 |

[a] The "modified stability ratio" (mS.R.) is defined in the text. [b] The literature values were taken from ref. 11. [c] These values were interpolated from a graphical plot of the data in column two against the best known literature values in column three. The estimated probable error is about ±0.1–0.2 e.v.

Evaluation of $E_A$.—The model envisioned for the proposed charge-transfer interaction is one in which the transfer occurs from the highest energy-filled orbital of the diazonium donor to the lowest energy vacant orbital of the chlorine ligand in the metal–complex acceptor. For this reason it is not expected that $E_A$ will be much different from that of chlorine. However, a more realistic estimate can be made by considering that $E_A$ is essentially that of chlorine increased by the electron affinity of the centered metal atom, appropriately weighted with respect to the numbers of chlorine ligands involved. Since for some of the metals involved here the electron affinities required in this procedure are not known, they were estimated by comparing the reported[11a] electron affinities for a few of the elements to their electronegativities (stability ratios, S.R.) defined on Sanderson's scale.[11b] Since a plot of the known approximate electron affinities of Cu, Zn, Cd, Sb, Sn, and Te *vs.* (mS.R.)[12] was essentially linear, the electron affinities of Fe, Mn, Co, and Bi could be estimated by interpolation. The resulting values are given in Table I. The

(7) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

(8) G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

(9) L. E. Lyons, *J. Chem. Soc.*, 5001 (1957).

(10) D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **34**, 2026 (1961).

(11) (a) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955) (especially appendix VII); (b) R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960, Chapters 2 and 3.

(12) Actually a modified stability ratio (mS.R.) was used. This is defined in exactly the same way as the known Sanderson stability ratio except the actual covalent radii of the atoms are used in calculating the electron densities rather than a hypothetical nonpolarized atomic radius.
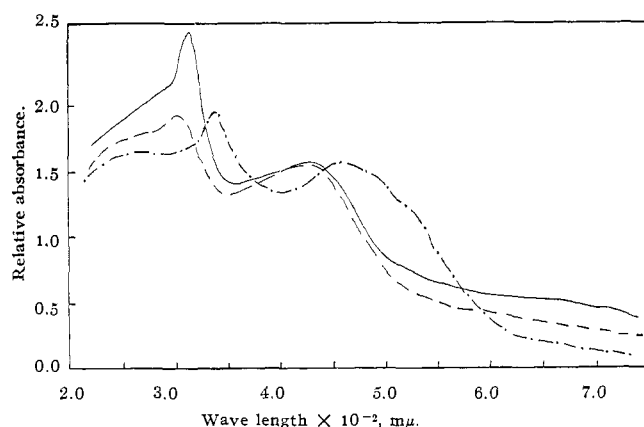
Fig. 2.—Some typical ultraviolet–visible reflectance spectra of diazonium salt complexes: ———, DzCl; – – – –, $(Dz)_2MnCl_4$; $\cdot—\cdot—\cdot—$, $(Dz)SbCl_6$.

final $E_A$ values for the metal chloro complex acceptors are presented in Table II.

Evaluation of $\Delta_{ic}$.—The fractional ionic character between the donor and the acceptor were also estimated from stability ratio data according to the procedure given in reference 12. The empirical equation, (S.R.) = 0.362 (mS.R.) + 0.286, relating the modified stability ratio (mS.R.) to the Sanderson stability ratio (S.R.) was employed. The fractional ionic character of the donor is then given approximately by the expression

$$\Delta_{ic} \simeq \frac{(S.R.)complex - (S.R.)donor}{2.08(S.R.)^{1/2}donor}$$

These values are also listed in Table II.

Evaluation of $r_{DA}$, $S_{DA}$, and $\beta$.—The average equilibrium distance, $r_{DA}$, between donor and acceptor was approximated as the mean of the effective π-radius, $\bar{r}_\pi$, for the diazonium cation (as determined from diamagnetic anisotropy data given in part I), the average radius of the complex anion, $\bar{r}_A$. The $\bar{r}_A$ values were taken as the geometrical mean of the M–Cl bond lengths in the various anion complexes.

The donor–acceptor overlaps, $S_{DA}$, were estimated from the empirical relationship proposed by Venkateswarbu and Jaseja[13] for two centered systems

$$S_{DA} \approx [0.21e^{-2|r_\pi - r_A|}]^{1/2}$$

The use of such a relationship seems justified for a rough estimate, since there are involved two orbitals (one from the donor and another from the acceptor) each of which refers to its own common center.

Finally, $\beta$ is approximated to the ionic resonance energy, which is given by $|\beta| \approx |X_D - X_A|^2$, where $X_D$ and $X_A$ are the Pauling electronegativities of the donor and acceptor, respectively. The $X$'s were determined from the modified stability ratio values through use of the empirical relationship, $X \simeq [0.076 (mS.R.) + 0.83]^2$, with an estimated over-all error of about ±6%. The final values obtained for $e^2/r_{DA}$, $S_{DA}$, and $\beta$ are given in Table II.

## Results and Discussion

In Fig. 1 three curves typical of the solution spectra of these compounds are present. Except for some differences in the intensities of the observed peaks, owing to the difficulty in maintaining equal solute concentrations, there are no important variations to be noted in these or any of the other solution spectra. The band at 380 mμ is characteristic of the diazonium group and the peak appearing at 245 mμ is peculiar to *p*-dimethylaminobenzenediazonium chloride and has been attributed to an intramolecular charge transfer from the diazonium group to the amino substituent.[14] However, the three curves appearing in Fig. 2 are typical of the solid state spectra as determined by reflectance methods. It is noted that the solid state spectra are considerably different from those observed in solution, and furthermore each of the spectra of the ten complexed diazonium compounds shows marked deviation from the pure diazonium salt alone. The

(13) P. Venkateswarbu and T. S. Jaseja, *Proc. Indian Acad. Sci.*, **44A**, 72 (1956).

(14) R. H. Nuttall, E. R. Roberts, and D. W. A. Sharp, *Spectrochim. Acta*, **17**, 947 (1961).

Table II

Calculated Charge-Transfer Spectra of Diazonium Salt Complexes[a]

| Compound | $I_D$, e.v. | $E_A$, e.v. | $-\beta$, e.v. | $\Delta_{ic}$ | $S_{DA}$ | $e^2/r_{DA}$, e.v. | $\lambda_{CT}$, m$\mu$ (theory)[b] | $\lambda_{CT}$, m$\mu$ (obsd.)[c] |
|---|---|---|---|---|---|---|---|---|
| DzCl | 7.0 | 3.78 | 0.5 | 0.11 | 0.35 | 5.93 | 210–265 | 215–300 |
| (Dz)FeCl$_4$ | 7.0 | 3.48 | 0.8 | .20 | .18 | 3.94 | 490–600 | 470–650 |
| (Dz)$_2$MnCl$_4$ | 7.0 | 3.92 | 1.2 | .40 | .16 | 3.84 | 225–245 | 225–275 |
| (Dz)$_2$CoCl$_4$ | 7.0 | 3.73 | 0.8 | .27 | .17 | 3.86 | 370–450 | 335–375 |
| (Dz)CuCl$_3$ | 7.0 | 3.5 | 0.8 | .20 | .19 | 4.03 | 460–560 | 440–575 |
| (Dz)$_2$ZnCl$_4$ | 7.0 | 4.08 | 1.2 | .40 | .18 | 4.00 | 210–225 | 210–275 |
| (Dz)CdCl$_3$ | 7.0 | 4.06 | 1.2 | .28 | .16 | 3.84 | 265–295 | 210–275 |
| (Dz)SbCl$_6$ | 7.0 | 3.40 | 1.2 | .20 | .14 | 3.74 | 460–560 | 470–650 |
| (Dz)BiCl$_4$ | 7.0 | 3.48 | 1.2 | .29 | .15 | 3.85 | 340–415 | 330–350 |
| (Dz)$_2$SnCl$_6$ | 7.0 | 3.56 | 1.2 | .40 | .16 | 3.84 | 275–300 | 265–300 |
| (Dz)$_2$TeCl$_6$ | 7.0 | 3.43 | 0.8 | .27 | .14 | 3.74 | 395–470 | 375–450 |

[a] The values reported for the theoretical calculations in this table are only semiquantative empirical estimates, and are at best accurate to only about 10%. The significance of the symbols used for the various quantities is given in the text. [b] Because of the uncertainty in the values used for the calculations, a spread in the calculated wave lengths of the charge transfer absorption maxima is given. These include the maximum probable error. [c] Since in many cases the observed spectra show only spectral shifts, shoulders, etc., and no true absorption maxima can be established for the charge-transfer effects, the entire regions for the specified absorptions are given.

fact that the solution spectra are consistent in displaying no variations on comparison of the various complexes is in agreement with past investigations, wherein both solution spectra and conductivity studies indicate that in solution the complexes are highly dissociated into separate anionic and cationic species and do not interact as a single complex.

Since broad, low intensity peaks shifted to longer wave lengths are general characteristics of reflectance spectra, the two maxima occurring at 425 and 315 m$\mu$ in DzCl are undoubtedly due to the diazonium group and the intramolecular charge transfer process, respectively, which are observed at 380 and 245 m$\mu$ in solution. Although the essential features of these two characteristic peaks remain in all of the complex salts, there are some additional features to be noted. For example, in DzCl, there is a rather steep region of absorption occurring in the 210–300 m$\mu$ region approaching the 315 m$\mu$ band. Within the limits of error of the present calculations, there should be a charge-transfer band occurring somewhere in the 210–265 m$\mu$ region. Similarly, in (Dz)$_2$MnCl$_4$ there is a blue shift of the 315 m$\mu$ peak with a rather broad shoulder in the 225–275 m$\mu$ region. This cannot be due to the Dz$^+$ ion itself, but may be partially due to the MnCl$_4$$^{-2}$ ion[15] and a charge-transfer interaction in the (Dz)$_2$MnCl$_4$ complex. The principal maxima of the MnCl$_4$$^{-2}$ ion occurring at about 430 and 450 m$\mu$ are of course completely masked by the broad 425 m$\mu$ band of the diazonium ion. The present calculations indicate that the proposed charge-transfer interaction should occur in the 225–245 m$\mu$ region.

Such comparisons as those given above can be made in the spectra of all the compounds studied. In every

case it is found that there is an anomaly that is best accounted for by the proposed charge-transfer interaction. In most cases these are manifested by significant shifts or an added shoulder in one of the observed bands. Consequently, we give only the regions in which the proposed charge transfer is observed rather than specify one single peak. Similarly in the calculated data, only those regions of charge transfer containing the maximum probable limits of error are presented. The final results of the observed and the calculated spectra are presented in the last two columns of Table II.

In conclusion, it appears that at least the qualitative aspects of the absorption spectra can be accounted for by the present semiempirical calculations. The calculated regions for charge transfer, assuming a model in which the diazonium component is the donor and the metal chloro complex species the acceptor, seem reasonably consistent with the observed spectra of all the compounds studied. Although it is not impossible that other electronic effects may be contributing factors, it does not seem likely that the apparent qualitative agreement between theory and experiment for all of these compounds could be merely coincidental. It is hoped that more extensive and comprehensive spectral investigations on single crystals of these and related compounds will yield more conclusive data. Such an approach would, however, involve a very tedious long-termed project requiring a very careful and accurate spectral analysis of both the complex anion and cation in each of the compounds studied.

(15) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **84**, 167 (1962).