Table III

ΔH and ΔS for Over-all Reaction and for the Dehydrogenation Part

Temp., °K.	$-\Delta H_{over\text{-}all}$, kcal.		$\Delta S_{over\text{-}all}$, Gibbs/mole		$-\Delta H_d$,[a] kcal.		$-\Delta S_d$,[b] Gibbs/mole	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
525.7	25.9	26.1	37.2	37.3	27.2	27.4	2.2	2.1
552.5	25.9	26.1	37.2	37.3	27.1	27.3	2.4	2.3
582.7	25.9	26.1	37.2	37.3	26.9	27.1	2.7	2.6

[a] $\Delta H_d = \Delta H_{i\text{-}C_4H_8} - \Delta H_{i\text{-}C_4H_{10}}$.   [b] $\Delta S_d = \Delta S_{i\text{-}C_4H_8} - \Delta S_{i\text{-}C_4H_{10}}$.

to each other, but the experimental K_p values are from 6 to 12% higher than those calculated.

Being given a small correction, each K_p value is recalculated to a common temperature and listed in Table II. The free energy changes of the reaction calculated from the K_p values are shown in the third column and these values, ΔF_{obsd}, are about 0.1 kcal. smaller than ΔF_{calcd} values which are calculated from thermodynamic data of the reactants and products.

From the average values of ΔF_{obsd} at the common temperatures, ΔH and ΔS of the reaction are found to be 25.9 ± 0.3 kcal. and 37.2 ± 0.6 e.u., respectively. The errors indicated are estimated from the accuracies of the quantities determined. These values of ΔH and ΔS give the following equation as the best fit of the experimental K_p values

$$\log K_p(\text{atm.}) = -(25900 \pm 300)/4.575T + 8.130 \quad (1)$$

In Table II we list the value of K_p calculated from this equation. The mean deviation from the average observed values is ±1%.

The thermodynamic quantities corresponding to $2HI - I_2$ are calculated from those of HI and I_2 and given in the 5th, 6th, and 7th columns. From ΔF_{obsd} for the reaction and $\Delta F_{(2HI - I_2)}$, $\Delta F_{i\text{-}C_4H_8} - \Delta F_{i\text{-}C_4H_{10}}$ (we define as ΔF_d) is determined and shown in the 8th

column. On the other hand, ΔF_d can be calculated directly from the thermodynamic data for $i\text{-}C_4H_8$ and $i\text{-}C_4H_{10}$. Comparing these ΔF_d values, the temperature dependence is almost identical for both observed and calculated. The observed values are about 0.10 kcal. higher than calculated ones. Although we feel that this is outside our own experimental error, it is well within the limit of error of the A.P.I. data.

In Table III we list the values of ΔH and ΔS calculated from the A.P.I. data along with the results of eq. 1. As can be seen, there is no temperature dependence for either in the range of interest and the results agree to within 0.2 kcal. for ΔH and 0.1 Gibb/mole for ΔS. The 3rd, 4th, 5th, and 6th columns of Table III show similar comparison with the ΔH_d and ΔS_d. The agreement between observed and calculated values are quite extraordinary.

Since the thermodynamic values for HI and I_2 are well known, the present technique gives values for the difference in entropies and enthalpies of any suitable paraffin and its related olefin in a temperature range where such data are either of poor precision or in many cases nonexistent. We hope to extend this technique to studies of other paraffin–olefin systems, to secondary alcohol–ketone systems, and to olefin–diolefin equilibria.

The Electric Moments of Two Dibenzobicyclooctadienes and Derivatives

By Dennis D. Tanner and Theodore S. Gilman

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The dipole moments of dibenzobicyclo[2.2.2]octadiene, dibenzobicyclo[3.2.1]octadiene, and some derivatives of the latter have been measured. These moments are compared with those calculated from theoretical models and tend to confirm the configurations assigned on the basis of chemical evidence. The Guggenheim–Smith method of calculating dipole moments from experimental data is compared with the Halverstadt–Kumler method.

Introduction

In the mechanism studies described by Cristol, Arganbright, and Tanner,[1,2] the hydrocarbons, dibenzobicyclo[3.2.1]octadiene (I) and dibenzobicyclo[2.2.2]octadiene (VIII) (hereafter referred to as ethanoanthracene), and various chloro and hydroxy derivatives of the former were prepared. In addition to the
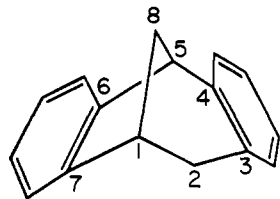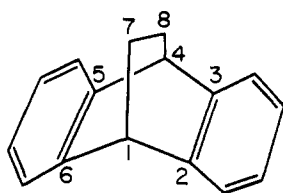
I   VIII

structural information deduced by them from chemical and kinetic evidence, it was desirable to have further supporting evidence for the assignment of configura-

tions to certain of the derivatives of I. A study of the electric dipole moments of the compounds was therefore undertaken. Furthermore, the bicyclic nature of these molecules gives rise to fairly rigid structures and thus makes possible the estimation of theoretical moments to compare with the experimental ones. This paper presents the experimental results of the dipole moment investigation and an attempt to calculate the moments from assumed models of the molecules studied.

Experimental

Materials.—The syntheses and properties of the compounds studied are described elsewhere.[1,2] Reagent grade benzene which had been refluxed over CaH_2 and fractionally distilled was used as the solvent for the compounds in the dielectric and refractometric measurements.

Apparatus.—The dielectric constants were measured with a heterodyne-beat apparatus similar to that described by Chien.[3] The variable oscillator was tuned with a precision capacitor (General Radio, Type 722-MD) for which a wormgear correction curve had been determined throughout its scale (0–1050 scale divisions). The change in capacitance caused by connecting the dielectric constant cell into the circuit or by changing the contents of the cell could be read with an uncertainty of ±0.05

(1) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, J. Org. Chem., 28, 1374 (1963).

(2) D. D. Tanner, Ph.D. Thesis, University of Colorado, 1961.

(3) J. Chien, J. Chem. Educ., 24, 494 (1947).

scale divisions. An absolute calibration of the precision capacitor was unnecessary since values of the dielectric constants were calculated from the ratios of corrected scale division readings.

Instead of tuning to zero beat between the fixed and variable oscillators, which can cause errors due to lock-in,[3] the variable oscillator was always tuned to a frequency of 1000 c.p.s. above the fixed oscillator, and this difference frequency was matched with the output of a 1000 c.p.s. vacuum-tube fork (General Radio, Type 723-C) on the display of an oscilloscope.

The cell used to measure dielectric constants was similar to one which has previously been described.[4] It was calibrated with specially purified benzene which had been fractionally crystallized several times, refluxed over CaH_2 for 16 hr., and fractionally distilled; $n^{25}D$ 1.4978 (cf. lit.[5] value of 1.49790). The value of the dielectric constant of this benzene was taken to be 2.2747[6] at 25°. The replaceable capacitance of the cell was about 208 pf. During measurements the cell was immersed in a constant-level water bath kept at 25.00 ± 0.03°.

Refractive index measurements (sodium D line) were made with a Pulfrich refractometer maintained at 25° by rapid circulation of water from the constant temperature bath. Since only changes in the square of the refractive index with concentration were needed in the dipole moment calculations, the micrometer screw settings were used directly to calculate these changes. Differences in refractive index as small as 10^{-5} unit can be detected with the micrometer.

Procedure.—Dielectric constant and refractive index measurements were made with dilute benzene solutions of the compounds studied. Solutions of each compound were prepared at five different concentrations which were roughly in the ratio of 5:4:3:2:1. Since the weights of the compounds available were as low as 90 mg. and since the cell volume was about 26 ml., it was necessary to make up solutions by diluting the original solution, rather than by preparing separate solutions at each concentration. The reliability of this dilution method was checked in two ways: (1) dilute solutions of chlorobenzene were run in this manner and (2) in one instance the solute was recovered by evaporation of the most dilute solution. The value of the dipole moment of chlorobenzene thus obtained (1.58 D.) was in good agreement with that obtained from measurements on separate solutions (1.59 D.), while the amount of solute actually recovered exceeded that calculated by only 1.1%. These two checks provided good evidence that solvent evaporation during the dilution manipulations had little effect on the correctness of the composition calculations.

The dilution technique was carried out as follows. Immediately after each dielectric measurement, a definite amount of the solution in the cell, as determined by marks on its outside, was expelled with dry nitrogen into a tared flask provided with a ground-glass stopper. The flask and contents were weighed before and after a predetermined amount of benzene had been added. The solutions studied had initial compositions ranging from 0.36 to 6.0 weight % polar solute. Sufficient amounts of each solution were saved for the refractive measurements. Dielectric and refractive data were also obtained for the solvent used in making up each set of solutions.

Calculations and Results

The dielectric constants of the solutions and of the solvent were calculated from the corrected precision capacitor readings and the replaceable capacitance of the cell. The change in the square of the refractive index with composition was evaluated from the change in the Pulfrich angle with weight fraction. Both the dielectric constant and refraction data were sufficiently linear when plotted against weight fraction to warrant a least squares determination for each compound of the slopes α and γ in the equations, $\epsilon_{12} - \epsilon_1 = \alpha w_2$ and $n_{12}^2 - n_1^2 = \gamma w_2$, in which the subscripts 12 and 1 refer to the solutions and solvent, respectively, ϵ and n are dielectric constant and refractive index, and w_2 is the weight fraction of the solute in the solutions.

Values of the molar orientation polarization at infinite dilution, $P_{2M,0}$, for each solute were calculated using the Guggenheim–Smith (G–S) relation[7,8]

(4) A. J. Petro, C. P. Smyth, and L. G. S. Brooker, J. Am. Chem. Soc., **78**, 3040 (1956).

(5) U. S. Department of Commerce, "Selected Values of Properties of Hydrocarbons," N.B.S. Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.

(6) A. S. Brown, P. M. Levin, and E. W. Abramson, J. Chem. Phys., **19**, 1226 (1951).

(7) E. A. Guggenheim, Trans. Faraday Soc., **45**, 714 (1949).

(8) T. W. Smith, ibid., **46**, 394 (1950).

$$P_{2M,0} = 3M_2v_1\left(\frac{\alpha}{(\epsilon_1 + 2)^2} - \frac{\gamma}{(n_1^2 + 2)^2}\right)$$

where M_2 is the molecular weight of the solute and v_1 the specific volume of the solvent. The electric moment values were calculated from the relation, which holds at 25°: μ (Debye units) $= 0.221(P_{2M,0})^{1/2}$.

Table I gives the measured values of α and γ, the orientation polarizations, and the dipole moments calculated therefrom (μ_{obsd}). The nature and stereochemistry of the substituents at the C_2 and C_8 positions on dibenzobicyclo[3.2.1.]octadiene (I) are indicated in the second and third columns. The syn stereochemistry at C_8 is taken to be that with the substituent pointing to the right with reference to the diagram for I. The estimated uncertainty in the observed moment values is no greater than ±0.2 D.

TABLE I

EMPIRICAL CONSTANTS, ORIENTATION POLARIZATIONS, AND DIPOLE MOMENTS AT 25°

No.	—Substituent at— C_2	C_8	α	γ	$P_{2M,0}$, cc./ mole	μ_{obsd}, D.	μ_{calcd}, D.
I	H	H	0.793	0.281	19.3	0.97	..
II	Cl(exo)	H	1.893	.284	72.2	1.88	1.74
III	H	Cl(syn)	1.661	.273	62.2	1.74	1.79
IV	Cl(exo)	Cl(syn)	4.893	.289	237.1	3.41	3.56
V	Cl(endo)	Cl(syn)	1.738	.272	76.9	1.92	2.47
VI	OH(exo)	H	1.468	.308	47.9	1.53	1.65
VII	OH(exo)	Cl(syn)	2.963	.304	129.7	2.50	2.74
VIII	Ethanoanthracene		0.670	.311	13.3	0.81	..

The G–S method of calculating orientation polarizations used here has not been employed as widely as the Halverstadt and Kumler (H–K) modification[9] of the Hedenstrand method.[10] It has the advantage over the H–K method in that it does not require density determinations and for this reason its use is inviting, particularly when only small amounts of solute are available. However, the G–S relation involves in its derivation the assumption that the ratio of the atomic polarizations of solute and solvent is the same as that of their molar volumes. This assumption has not been thoroughly tested because of the difficulty in obtaining atomic polarization data, but seems reasonable on an empirical basis as will be demonstrated below. On the other hand, the H–K method furnishes limiting values for the total polarization of the solute; therefore some assumption as to the magnitude of the distortion polarization of the solute, P_{2D}, has to be made in order to calculate the dipole moment. The usual procedure is to assume that P_{2D} equals the molar refraction (Na D line) of the solute, MR_D, or exceeds it by 5 or 10%.[11]

Data on the change in dielectric constant, density, and refractive index with composition afford a comparison of the H–K and G–S methods. Smith[8] cites data for aniline in benzene which yield dipole moments which differ by only 0.02 D. when calculated by the two methods and when P_{2D} is assumed to be 5% greater than MR_D in the H–K approach. T.S.G. has carried out similar calculations from measurements on solutions of chlorobenzene in benzene; the dipole moments so obtained were 1.59 and 1.60 D. for the H–K and G–S methods, respectively. It is perhaps to be expected that good agreement between the two methods would be obtained in the examples just cited since, when the electric moment is high (>1.5 D.), the term involving the change in dielectric constant with composition, α,

(9) I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., **64**, 2988 (1942).

(10) G. Hedenstrand, Z. physik. Chem., **2B**, 428 (1929).

(11) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 222.

which appears in both the H–K and G–S equations, is much larger than the terms involving the change in density and refractive index and hence largely determines the magnitude of the dipole moment. A more critical comparison of the two methods would therefore be obtained for a compound of rather low polarity in which the density and particularly the refractive terms are not outweighed by a large α term. We have made such a comparison, using the least polar of the compounds reported here, ethanoanthracene. The electric moment values obtained were 0.84 and 0.81 D. by the H-K and G–S methods, respectively.[12] We are thus led to believe that the G–S method employed in calculating the moments we are reporting is reliable, particularly when used to compare dipole moments computed from data which were all obtained in dilute solutions with a common solvent and at the same temperature.

Theoretical Moment Values.—In the absence of any direct structural information, it was first necessary to deduce a geometrical model of the parent hydrocarbon I from considerations of minimum strain in bond length and bond angle. A model for I was therefore derived in the following manner. Examination of a Dreiding stereo-model suggested that a reasonable structure would involve all of the carbon atoms lying in one of three planes. In accordance with the numbering system in the diagram for I given above, one of these planes included C_1 through C_5 and the right-hand benzene ring; another included C_1, C_5, C_6, C_7, and the left-hand benzene ring; and the third included C_1, C_5, and C_8. A right-handed Cartesian coordinate system for the molecule was therefore adopted in which the origin was the mid-point between C_1 and C_5, the z-axis being directed upward through C_5, and the x-axis through C_1. The y-axis then pointed to the right.

The calculation of moment values for the derivatives of I studied was then undertaken in a manner analogous to that demonstrated for some bicyclic molecules by Wilcox.[13] The steps involved were: first, the assignment of the bond lengths and bond angles in the molecule consistent with minimum strain; second, the computation from the assigned structure of the coordinates of the carbon atoms of interest; and third, the evaluation of the components of unit bond vectors for the various substituent configurations.

The assignment of distances and angles was based on the following considerations. The primary features determining the geometry of the molecule are the 1–5 distance and the angle between the plane containing C_6 and C_7 and that containing C_8. The ring system on the left is the "tightest" because the bridgehead carbon atoms are *ortho* to each other relative to the left-hand benzene ring and are also joined by a methano bridge. The starting point was therefore to find angles and distances in the five-membered ring containing C_1, C_8, C_5, C_6, and C_7 which were consistent with reasonable values for the interplanar angle and for the bond angles at the bridgehead carbons. In this connection, the relation between bond angle and strain given by Hendrickson[14] was used. Once the 1–5 distance was decided upon, it was a fairly simple matter to find values for the angles and carbon–carbon distances in the right-hand ring system which were consistent with minimum strain in the ring itself and at the bridgeheads. The following table summarizes the angles and distances which appeared to be most reasonable.

(12) We are indebted to Mr. Clarence F. Hale, Jr., for making the density measurements needed in the H-K calculation.

(13) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(14) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

TABLE II

ASSUMED GEOMETRY OF MOLECULE I

Angles		Distances, Å.	
1–7–6 = 5–6–7 =	110.0°	1–2 = 2–3 = 4–5 =	1.55
1–8–5 =	102.6°	3–4 = 6–7 =	1.39
7–1–8 = 6–5–8 =	96.5°	1–8 = 5–8 =	1.55
1–2–3 =	113.0°	1–7 = 5–6 =	1.51
2–3–4 = 3–4–5 =	121.0°	1–5 =	2.42
2–1–8 = 7–1–2 =	111.5°		

The angle between the planes containing the two bridges with benzene rings comes out to be 111°, as compared with the angle between the planes of the two-carbon bridges in norbornane and norbornadiene, which have been found to be 110 and 111°, respectively, by electron diffraction studies.[15] Furthermore in these same studies the angles between the double bonds and the bonds to the bridgeheads in norbornadiene were found to be 109.1°, which supports the choice of 110° for the angles 1–7–6 and 5–6–7 given in Table II.

With these parameters the coordinates of any of the carbon atoms in the molecule can be calculated. The coordinates of the carbons at which substitution can occur were in turn used to evaluate the components on the three-coordinate axes of unit vectors directed toward the nuclei of the substituent atoms bonded to these carbons. In computing these vector components, it was assumed (1) that the pairs of vectors directed toward the substituent atoms bonded *exo* and *endo* to C_2 or *syn* and *anti* to C_8 defined planes which were each perpendicular to the planes containing the respective ring systems in which the atoms C_2 or C_8 lay and (2) that the angles between these vectors in each pair departed from the tetrahedral angle of 109.5° by an amount equal and opposite to the amount by which the ring system angles about C_2 or C_8 departed from the tetrahedral value. Thus the angle between the *exo* and *endo* bond vectors was taken to be 106.0° and that between the *syn* and *anti* vectors 116.4°. These angles were assumed to be bisected by the planes of the respective ring systems.

Table III gives the coordinates calculated for C_2 and C_8 and the components of unit vectors for the various configurations at these positions.

TABLE III

COORDINATES OF C_2 AND C_8 IN MOLECULE I AND UNIT VECTORS

Atom	Coordinates			Unit vector components		
	x	y	z	x	y	z
C_2	1.35	1.35	−0.742	*exo* +0.530	+0.635	+0.562
				endo + .530	− .135	− .838
C_8	0.00	0.00	+0.969	*syn* .000	+ .850	+ .527
				anti .000	− .850	+ .527

The theoretical moments (μ_{calcd}) which are given in the last column of Table I were calculated by combining the proper unit vectors with the moment of the group involved, following the method of Wilcox,[13] and adding in the moment of the parent hydrocarbon, 0.97 D., which was assumed to be directed along the negative z-axis, *i.e.*, to have unit vector components of 0, 0, and −1. The net values for the C–Cl and C–O–H group moments were taken to be 2.1 ± 0.1[16] and 1.6 ± 0.1 D.,[17] respectively. The term "net" is used to imply that these group moments include

(15) V. Schomaker, unpublished data kindly furnished by Dr. Saul Winstein.

(16) This is approximately the dipole moment of cyclopentyl chloride which M. T. Rogers and J. D. Roberts (*J. Am. Chem. Soc.*, **68**, 843 (1946)) found to be 2.08 D. in benzene at 25°.

(17) H. Krieger and J. J. Lindberg (*Suomen Kemi.*, **B33**, 117 (1960)) measured the dipole moment of bicyclo[2.2.2]octanol-2 in benzene at 25°. The value obtained (1.57 D.) is assumed to represent the magnitude of the C–O–H group moment in a freely rotating condition.

the C–H group moment which is assumed to cancel out in the calculations. A typical calculation is given for compound IV of Table I.

$m_x = 2.1(0.530) + 2.1(0.000) + 0.97(0) = 1.11$

$m_y = 2.1(0.635) + 2.1(0.850) + 0.97(0) = 3.11$

$m_z = 2.1(0.562) + 2.1(0.527) - 0.97(1) = 1.32$

$\mu_{calcd} = (m_x^2 + m_y^2 + m_z^2)^{1/2} = [(1.11)^2 + (3.11)^2 +$
$$(1.32)^2]^{1/2} = 3.56 \text{ D.}$$

The theoretical moments for the two alcohols VI and VII were calculated assuming free rotation of the O–H group about the C–O bond axis. Such calculations required a modification of the Wilcox method[13] in that it was necessary to use equations which give each of the three unit vector components of the rotating group moment as a function of the angle of rotation. These equations have been derived elsewhere[18] and lead to the following equation for $\langle \mu^2 \rangle$, the mean value of the square of the resultant moment of a molecule containing a combination of one rotating polar group and one or more fixed polar groups

$$\langle \mu^2 \rangle = m^2 + m_1^2 + 2m_1(m_x a_x + m_y a_y + m_z a_z) \cos \phi \quad (1)$$

in which $m^2 = m_x^2 + m_y^2 + m_z^2$; m_1 is the scalar value of the rotating group moment; m_x, m_y, and m_z are the x, y, and z vector contributions of the fixed group moment(s), calculated as in the example given above; a_x, a_y, and a_z are the components of the unit vector directed along the axis of rotation; and ϕ is the angle between the axis of rotation and the rotating vector. In applying the above equation to the theoretical moments of VI and VII, the components a_x, a_y, and a_z were taken to be those of the exo bond at C_2 (Table III), and 1.6 and 63° were used for m_1 and ϕ, respectively. The value of 63° for the angle between the axis of rotation and the rotating vector was calculated from Smyth's data[19] for the C–O and O–H bond moments, assuming a C–O–H bond angle of 105°.[20]

Uncertainties in the moment of the hydrocarbon and of the substituent group, both about ±0.1 D., result in an uncertainty in the theoretical moments of approximately 5%. The effect of uncertainties in the structural parameters is difficult to assess, but of course can be serious if the model assumed differs significantly from the correct one.

Discussion

The structural assignments indicated in Table I on the basis of chemical evidence[1,2] are consistent with the observed dipole moments of the derivatives listed. For example, Tanner[2] has found evidence for the exo configuration of the chloride II and alcohol VI. The experimentally determined moments for these compounds agree with the values calculated within the limits of error, whereas the moments calculated for the endo isomers of II and VI with the aid of the vectors given in Table III and of eq. 1 are 2.96 and 2.16 D., respectively.

Though the good agreement between the experimental and theoretical moments does not in itself prove the syn configuration of the Cl atom in III, since according to the method of calculation the anti isomer of III would have the same moment, the moment values for the disubstituted derivatives do tend to confirm the syn configuration. Cristol, Arganbright, and Tanner[1] have presented chemical evidence that the isomeric pair of dichlorides obtained in the ionic chlorination of ethenoanthracene must have either the assigned configurations IV and V in Table I or those of their struc-

turally epimeric anti forms. The observed dipole moment values tend to confirm the assignments given, particularly for IV. For if one calculates theoretical moments for the anti isomers of IV and V, values of 1.78 and 2.84 D., respectively, are obtained. The observed moment for IV is in good agreement with that calculated for the syn isomer (see Table I), while the observed moment for V (1.92 D.), though significantly smaller than either of the theoretical moments, is closer to the value calculated for the syn isomer (2.47 D.) than to that of the anti (2.84 D.).

Distances between the nuclei of substituent atoms bonded directly to the bicyclic system can also be calculated if the coordinates of the carbon nuclei involved and the unit vectors are known.[18] Of particular interest here is the separation between the Cl atoms in IV. Using 1.77 Å. for the C–Cl bond length,[21] one can calculate that the Cl–Cl distance is 3.0 Å., which is less than twice the van der Waals radius of a Cl atom by 0.6 Å. Thus there should be to some extent a mutual inductive effect between the two C–Cl bond dipoles and/or a spreading of the angle between the two C–Cl bond vectors, either of which would cause a lowering of the moment for the molecule. In the same way the separation between the hydroxyl H and the syn-Cl in VII can be calculated for the conformation in which the H and Cl atoms are closest to one another. Using 1.43 and 0.96 Å. as the C–O and O–H bond lengths[21] and an oxygen valency angle of 105°,[20] one calculates this separation to be 2.1 Å.,[18] with an angle of about 26° between the O–H bond and a line joining the O and Cl nuclei. The sum of the van der Waals radii of an H and a Cl atom is 3.0 Å.[21] This suggests the possibility of a weak hydrogen bond to the Cl atom. However, when the moment of VII is calculated for such a conformation,[18] a value of 2.81 D. is obtained if inductive effects are neglected. This is slightly greater than the value calculated for free rotation and even greater than the observed moment. If, on the other hand, there is a steric repulsion between the hydroxyl H and the Cl atoms, such that the OH group is oriented away from the Cl, the calculated moment is 2.66 D.,[18] which is closer to the observed moment of 2.50 D.[22] Thus, in view of the uncertainties in both the experimental and theoretical moment values, it is clear that no conclusion can be drawn from these data as to whether the OH group is freely rotating or whether it assumes some particular orientation with respect to the rest of the molecule.

The observed moment for ethanoanthracene (VIII) can be accounted for on the basis of a model in which a dihedral angle of 110 to 120° and a value of 110° for the angles 1–2–3, 2–3–4, 4–5–6, and 5–6–1 are assumed. With all single and aromatic C–C bonds assumed to have distances of 1.54 and 1.39 Å., respectively, these angles appear to give the least strained conformation for the molecule. The over-all moment (0.81 D.) can thus be thought of as the resultant of the moments of two distorted o-xylyl groups whose planes make an angle of 110 to 120° with each other. This is turn means that each o-xylyl group has a moment of 0.70 to 0.81 D. The distortion arises in that the angles 1–2–3, etc., are assumed to be 110° instead of 120°. Thus the angle between the two bond vectors directed from the bridgeheads toward the adjacent carbons in either ring is 40°, from which one calculates the moment of a single bridgehead to ring bond to lie between 0.37 and 0.43 D. This range of values is consistent with the dipole mo-

(18) T. S. Gilman, to be published.

(19) C. P. Smyth, ref. 11, pp. 301–302.

(20) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, N. Y., 1960, p. 453.

(21) L. Pauling, ref. 18, Chapter 7.

(22) Infrared studies with this compound showed no evidence for intramolecular hydrogen bonding (S. J. Cristol and D. D. Tanner, unpublished data).

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 ethano-anthracene (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-Dimethylamino-benzenediazonium Chloride. II. Spectral Studies

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The qualitative aspects of charge-transfer spectra anticipated in complexes of p-dimethylaminobenzene-diazonium 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]: $(Dz)FeCl_4$, $(Dz)_2MnCl_4$, $(Dz)_2Co-Cl_4$, $(Dz)CuCl_3$, $(Dz)_2ZnCl_4$, $(Dz)CdCl_3$, $(Dz)SbCl_6$, $(Dz)BiCl_4$, $(Dz)_2SnCl_6$, 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 MgCO₃ 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

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

(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).

where ψ_N is the complete wave function for the ground state of the complex, ψ_0 the "no bond" function, and ψ_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 $\int \phi_D \phi_A d\tau$, ϕ_D being the highest energy filled orbital of the donor and ϕ_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 β the resonance integral. Thus ΔW 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 ΔW 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 Δ_{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, Δ_{ic}, S_{DA}, r_{DA}, and β, 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

(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).