[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, KANSAS STATE COLLEGE AND UNIVERSITY OF MARYLAND]

Normal Coördinate Analysis and Aromatic Character of Five- and Seven-membered Aromatic $(CH)_n$ Rings

BY RICHARD D. NELSON,[1] WILLIAM G. FATELEY[1] AND ELLIS R. LIPPINCOTT

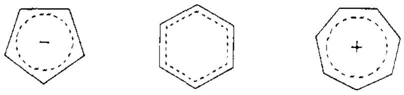
RECEIVED MAY 14, 1956

The results of a normal coördinate analysis of the vibrational spectra of five- and seven-membered $(CH)_n$ aromatic rings are given and compared with similar calculations for benzene. The assignment of frequencies used was based on infrared and Raman spectral studies of the tropylium ion in cycloheptatrienyl bromide and of the cyclopentadienyl rings in ferrocene and related compounds. The valence force symmetry coördinates for C_5H_5 and $C_7H_7^+$ agree reasonably well with those for benzene given by Crawford and Miller indicating that the delocalization of 6π electrons in five-, six- and seven-membered rings is the dominant factor in determining the type of vibrational potential function.

Introduction

Chemical and physical evidence indicates that the cyclopentadienyl rings in ferrocene and related compounds have a considerable amount of aromatic character due to the delocalization of the π electrons.[1-9] X-Ray diffraction, electron diffraction and spectroscopic techniques have demonstrated the equivalence of all 5 CC bonds and CH bonds in the cyclopentadienyl rings.

The recent synthesis of tropylium bromide by Doering and Knox was followed by studies of its chemical and physical properties which demonstrate conclusively that the tropylium ion is a new aromatic system the relative stability of which is due to resonance resulting from the presence of six (π) electrons in the conjugated unsaturated seven membered ring.[10,11]



The earliest quantum mechanical analysis of aromatic systems has described their stability in terms of the presence of six (π) electrons rather than the size of the ring system with the result that the cyclopentadienyl anion and cycloheptatrienylium (tropylium ion) cation should have aromatic properties similar to benzene.[12] The quantum mechanical analysis is conveniently summarized by the $2 + 4n$ rule for stable aromatic molecules.

$$\pi \text{ electrons} = 2 + 4n$$
$$n = 0, 1, 2 \ldots$$

The rule gives the number of π electrons necessary for filled (stable) orbitals in terms of the angular momentum quantum number for electronic motion about the center of the ring.[13]

The vibrational spectra of the cyclopentadienyl rings in ferrocene and other metal cyclopentadienyl compounds as well as that for the tropylium ion contain features which are quite similar to spectral features in the vibrational spectrum of benzene.[8,11] However, there are a number of differences in the spectra of five-, six- and seven-membered aromatic ring systems such as the position of the ring breathing and ring distortion frequencies. The former occurs at 1105 cm.$^{-1}$ for a cyclopentadienyl ring and at 868 cm.$^{-1}$ for a tropylium ion ring. The latter occurs at 885 and 433 cm.$^{-1}$ respectively, for the five- and seven-membered rings. The question arises as to the extent to which these differences may be associated with geometrical factors involving ring size and the extent to factors which result from differences in the electronic configuration of the five-, six- and seven-membered aromatic ring system. One approach to this problem is to compare the corresponding potential constants resulting from a normal coördinate analysis of the vibrational spectrum of each ring system. A comparison of these force constants should furnish, to a good approximation, similarities or differences which are independent of geometrical factors.

We have recently completed a normal coördinate analysis of the vibrational spectra of the tropylium ion $C_7H_7^+$, and the cyclopentadienyl ring C_5H_5. The analysis is based on detailed Raman and infrared spectroscopic studies of ferrocene, $Fe(C_5H_5)_2$, ferrocene-d_{10}, $Fe(C_5D_5)_2$, ruthenocene, $Ru(C_5H_5)_2$ and tropylium bromide, C_7H_7Br. A detailed description of the normal coördinate analysis will be given with publication of the separate spectroscopic studies. We are presenting here the results of these calculations with a comparison to similar calculations for benzene.

Normal Coördinate Analysis.—The normal coördinate analysis was carried out by methods similar to those used by Crawford and Miller[14] for benzene using the Wilson FG matrix technique.[15] The tropylium ion, $C_7H_7^+$, has D_{7h} symmetry while a cyclopentadienyl ring has D_{5h} symmetry. The selection rules and types of modes of vibration are

---

(1) Portion of a dissertation presented as partial fulfillment of the requirement for the degree of Doctor of Philosophy in Chemistry at Kansas State College.

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

(3) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, **74**, 2125 (1952).

(4) E. O. Fisher and W. Pfab, *Z. Naturforsch.*, **7b**, 377 (1952).

(5) W. Pfab and E. O Fisher, *Z. anorg. Chem.*, **274**, 317 (1953).

(6) R. F. Eiland and D. Pepinsky, THIS JOURNAL, **74**, 4971 (1952).

(7) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

(8) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953); THIS JOURNAL, **77**, 4990 (1955).

(9) For a review of ferrocene and related compounds see P. L. Parson, *Quart. Rev.*, **10**, 391 (1955).

(10) W. von E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

(11) W. G. Fateley and E. R. Lippincott, *ibid*, **77**, 249 (1955).

(12) E. Hückel, *Z. Physik*, **70**, 204 (1931), "Grundzuge der Theorie ungesattigter und aromatische Verbindungen," Verlag Chemie, Berlin, 1938, pp. 71–85.

(13) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, pp. 134–149.

(14) B. L. Crawford and F. Miller, *J. Chem. Phys.*, **14**, 282 (1940); *ibid.*, **17**, 249 (1949).

(15) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

summarized in Table I along with those for benzene. A study of the selection rules shows that despite the different symmetry and numbers of atoms present in five-, six- and seven-membered planar $(CH)_n$ rings, the selection rules predict the same number and types of active fundamental frequencies in the infrared and Raman spectra. This is a general rule for $(CH)_n$ planar rings for $n \geq 5$.[16]

TABLE I

SELECTION RULES AND TYPES OF VIBRATIONS FOR AROMATIC FIVE-, SIX- AND SEVEN-MEMBERED $(CH)_n$ RINGS

Symmetry species D_{5h} C_5H_5	D_{6h} C_6H_6	D_{7h} $C_7H_7^+$	Spectral activity[a]	No.[c]	Description[b]
A_1'	A_{1g}	A_1'	Raman	1	CH stretching
			Raman	2	Ring breathing
A_2''	A_{2u}	A_2''	Infrared	4	CH(⊥) bending
E_1''	E_{1g}	E_1''	Raman	11	CH(⊥) bending
E_1'	E_{1u}	E_1'	Infrared	12	CH stretching
			Infrared	13	CC stretching
			Infrared	14	CH(||) bending
E_2'	E_{2g}	E_2'	Raman	15	CH stretching
			Raman	16	CC stretching
			Raman	17	CH(||) bending
			Raman	18	CCC(||)bending

[a] Inactive fundamentals are not tabulated. [b] (⊥) and (||) indicated modes of vibration which are perpendicular and parallel to the plane of the ring, respectively. [c] The numbering system used here for the active modes is the same as that used for benzene.

For each symmetry species secular equations of the form

$$|F - \lambda G^{-1}| = 0$$

were set up and solved by using the appropriate symmetry coördinates and geometric data. Here F represents the force constant matrix, G the kinetic energy matrix and $\lambda_i = 4\pi^2c^2\omega_i^2$. The method furnishes valence force symmetry constants (VFSC) and not valence force constants (VFC). In order to make the problem tractable all off-diagonal force constants were assumed to be zero except $F_t\beta$ in species E_1' and E_2'. The assignment of frequencies used in the analysis is listed in Table II. The numbering of active frequencies for the five- and seven-membered rings is the same as that used for benzene. For degenerate species E_1' and E_2' the solution of the cubic and quartic secular equations was preceded by factoring the CH stretching force constant by the method of Wilson.[15] The error involved is negligible since the CH stretching frequencies are much larger than the other frequencies in these species.

The results of the normal coördinate analysis for the tropylium ion and cyclopentadienyl rings are given in Table II along with the VFSC constants obtained by Crawford and Miller, for benzene. The three sets of VFSC constants are similiar. The main effect of the metal bonding to the ring in $Fe(C_5H_5)_2$ appears in the lowering of multiple bond CC force constants. With the possible exception of the CC(||) bending constant, a comparison of the three sets of constants shows that the main reason for the difference in the vibrational spectra of five-, six- and seven-membered aromatic rings is due to geometric factors and ring size and not to large variations of the force constants. Thus the delocalization of six π electrons in five-, six- and seven-membered rings appears to be the overriding factor in determining the vibrational motion and results in approximately the same set of potential constants for each ring. Indeed we have found it possible to transfer the VFSC constants of benzene into the secular equations for the vibration motion of $C_7H_7^+$ ion and have predicted its infrared and Raman spectra with little error.

TABLE II

COMPARISON OF VALENCE FORCE SYMMETRY CONSTANTS FOR THE CYCLOPENTADIENYL, TROPYLIUM ION AND BENZENE RINGS

Type	No.[a]	(C_5H_5), cm.$^{-1}$	C_6H_6, cm.$^{-1}$	$(C_7H_7^+)$, cm.$^{-1}$	$(C_2H_5)^-$ VFSC, dynes/cm.	C_6H_6[b,c] VFSC,	$(C_7H_7^+)$[c,d] VFSC,
CH stretching	1	3099	3062	3060	4.99×10^5	5.12×10^5	5.16×10^5
CC stretching	2	1105	992	868	6.97×10^5	7.62×10^5	7.66×10^5
CH(⊥) bending	4	811	671	633	0.42×10^{11}	0.228×10^{11}	0.256×10^{11}
CH stretching	12	3085	3099	3020	5.18×10^5	5.15×10^5	5.00×10^5
CC stretching	13	1411	1485	1477	5.50×10^5	6.14×10^5	7.40×10^5
CH (||) bending	14	1002	1037	992	0.96×10^{-11}	1.02×10^{-11}	0.96×10^{-11}
CH stretching	15	3085	3047	3075	5.218×10^5	5.04×10^5	5.18×10^5
CC stretching	16	1560	1596	1594	5.50×10^5	5.66×10^5	6.09×10^5
CH(||) bending	17	1178	1178	1210	0.95×10^{-11}	0.99×10^{-11}	1.16×10^{-11}
CC(||) bending	18	885	606	433	1.78×10^{-11}	1.45×10^{-11}	1.02×10^{-11}

[a] Frequency number 11, the Raman active CH bending mode, was not observed in the spectra and the corresponding force constant was not calculated. [b] B. L. Crawford and F. Miller, *J. Chem. Phys.*, **17**, 249 (1949). [c] Stretching and bending VFSC are in units of dynes/cm. and dynes-cm. respectively. [d] For $C_7H_7^+$ the $F_t\beta$ interaction constant has values of $2.36 \cdot 10^{-3}$ dyne and $0.22 \cdot 10^{-3}$ dyne in species E_1' and E_2', respectively. For C_5H_5 the $F_t\beta$ interaction in species E_1' has a value of $2.10 \cdot 10^{-3}$ dyne.

An examination of the variations of corresponding force constants as one passes from a seven-membered to five-membered ring shows some trends. The C–C constants tend to become slightly smaller. The C–C–C planar angle bending constant in species E_2' becomes larger. The CH out of plane constant in species A_2'' becomes slightly larger. We attribute part of this effect to the bonding of the cyclopentadienyl rings to the metal atoms in the molecules $M(C_5H_5)_2$. The dif-

---

(16) A corollary of this rule is that the vibrational spectra of $C_3H_3^-$, $C_3H_3^+$ and C_4H_4 aromatic ring systems will differ significantly from those of the $C_5H_5^-$, C_6H_6 and $C_7H_7^+$ aromatic systems solely on symmetry grounds. Since the former systems are not known it is interesting that there is a correlation between the stability of aromatic systems and the type of selection rules predicted from the symmetry of the ring system.

ferences between the constants for the six- and seven-membered rings may not be significant. We have examined our results in terms of the variations of bond order in five-, six- and seven-membered aromatic rings but have been unable to find any definite correlation.

MANHATTAN, KANSAS
COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

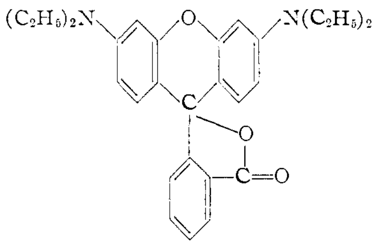
Rhodamine B Equilibria

BY R. W. RAMETTE[1] AND E. B. SANDELL

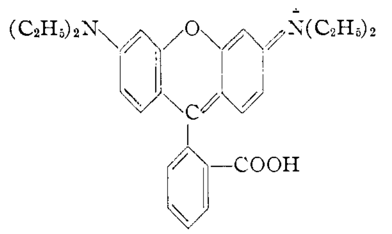
RECEIVED FEBRUARY 20, 1956

An investigation of rhodamine B (R) equilibria included a benzene extraction study, measurement of solubility of R salts and a spectrophotometric study in aqueous solution. The colorless lactone form (R°) undergoes a separation of charges in polar solvents to form an intensely colored violet zwitterion (R^{+-}). R^{+-} can add a proton to the carboxyl group formed by the opening of the lactone ring, giving RH^+ which has nearly the same absorption spectrum as R^{+-}. Addition of a second proton, probably to one of the nitrogen atoms, yields an orange species RH_2^{++}. A third proton gives RH_3^{+++}, which is yellow. The color changes are explained in terms of canonical structures. The cations are capable of interaction with anions such as chloride, bromide and perchlorate in solution to form ion pairs having the same absorption spectra as the free cations. In addition, R^{+-} and ion pairs containing RH^+ or RH_2^{++} undergo dimerization as the concentration is increased, causing an apparent deviation from Beer's law. Most of the equilibrium constants were determined.

The preparation, purification and chemical structure of rhodamine B (C.I. 749) were reported by Noelting and Dziewonski.[2] They concluded that the two principal forms of the dye were the lactone (R°)



and a salt form (RHCl)



The present work shows that several other forms exist in solution in equilibrium.

Apparatus.—Qualitative studies of absorption spectra were made with a Cary Model 11 Recording Spectrophotometer. Special adapters were machined to permit the use of rectangular cells. Quantitative measurements of absorbance were made with a Beckman Model B spectrophotometer. The 10 cm. cells were cylindrical with silica windows. The 1 cm. cells were Pyrex. Also used were Beckman cell-spacers, which are 9 mm. blocks of quartz designed to reduce the light path of 1 cm. cells to 1 mm. They are supplied with two polished sides, the other sides and bottom being ground. It was found that the ground sides strongly adsorbed rhodamine B from solution, causing erratic results. To eliminate this difficulty the rough sides were polished. A mechanical shaker was used to establish equilibrium in the two-phase systems. A Beckman Model H *p*H meter was used for *p*H measurements.

Reagents.—Rhodamine B chloride was purified by adding slowly, with stirring, about ten volumes of anhydrous ether to a saturated solution of the dye in absolute ethanol. The salt precipitated in the form of golden-green flakes. The process was repeated and the filtered solid was washed with ether and air-dried. The absorptivity of the purified dye in an ammonia–ammonium chloride buffer, the procedure proposed by Dolinski[3] for analysis of commercial preparations of the dye, was about 5% greater than that of the original. Amperometric titration of chloride with silver nitrate, using a rotated platinum electrode, indicated a purity of 99%.

Rhodamine B bromide was prepared by addition of 2 *M* potassium bromide to a saturated solution of the chloride in water. It was purified in the same manner as the chloride.

Rhodamine B perchlorate was prepared analogously. All three salts were of similar appearance except that the particles of the perchlorate tended to be much smaller because of its very low solubility.

All other chemicals were reagent grade.

Qualitative Spectrophotometric Study.—Figure 1 shows the absorption spectra of very dilute solutions of the dye as a function of acidity. It is seen that there are four distinct species in aqueous solution. Curve 1 is the spectrum of the violet form used by Dolinski and is representative of solutions having *p*H values from 13 to 4. Curve 2 is virtually identical to curve 1, except that there has been a 3 mμ shift toward longer wave lengths. This slight change is not observable visually. The species responsible for this spectrum is the principal one in the *p*H range from 3 to 1. Curve 3 is the spectrum of an orange form which is the main constituent in solutions of *p*H 0 to −1. Curve 4 is characteristic of a yellow form fully present only in concentrated sulfuric or perchloric acid, and virtually absent in aqueous solutions of less than 6 *M* acidity. Curve 5 is the spectrum of a colorless benzene solution of the dye, prepared by extraction of a neutral water solution.

Curves 1–3 change shape when the concentration of the dye is increased. Figure 2 shows this concentration effect for solutions of *p*H 8 and −0.6 corresponding to curves 1 and 3 of Fig. 1. The effect on curve 2 of Fig. 1 is very similar to that shown in Fig. 2 for *p*H 8.

Discussion

The qualitative observations, coupled with the quantitative results to be described, lead to the fol-

---

[1] Carleton College, Northfield, Minnesota. From the Ph.D. thesis of R. W. Ramette, 1954.

[2] E. Noelting and K. Dziewonski, *Ber.*, **38**, 3516 (1905).

[3] M. Dolinski, *J. Assoc. Offic. Agr. Chem.*, **32**, 130 (1949).