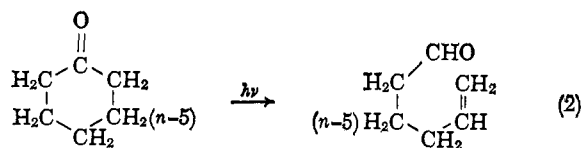


0.5% of cyclohexanone. If this is due to a quenching reaction between the 5-hexenal and excited cyclohexanone, it must not extend to the excited state which undergoes reaction 1. On this basis, while it is not possible to identify the states, it can at least be said that two different electronically excited states must be responsible for the formation of 5-hexenal and 2-methylcyclopentanone in the condensed phase. The decrease in the yield of both isomers on the addition of increasing amounts of cyclohexane is probably due to a photoaddition reaction between cyclohexanone and the solvent.¹⁸

In every one of the monocyclic ketones that were studied, the well-known photoisomerization reaction which leads to unsaturated, open-chain aldehydes was also observed. A few comments on this reaction which, in general, can be written as



can be made from the new data that were obtained in the present study. The probable mechanism of this

(18) At first sight, it may seem surprising that the photoaddition reaction between cyclohexanone and solvent is not replaced in the pure liquid by an equally efficient bimolecular process between two ketone molecules. However, a collision between an excited ketone molecule and another ketone molecule may lead to energy transfer without addition, at least some of the time. Even in the pure liquid, the isomerization products are formed only in poor yield compared to the condensation products.

reaction has already been suggested to be a transfer of the hydrogen atom from the β - to the carbonyl carbon before or at the same time as the ring is broken.⁶ In line with this, it was found that the aldehyde from 2-methylcyclohexanone was exclusively *trans*-5-heptenal. The uncertainty concerning the peak at 756 cm^{-1} that was reported earlier¹⁰ has now been removed. The aldehydes from 2-*n*-propylcyclopentanone and 2-ethylcyclopentanone have also been found¹⁹ to be exclusively the *trans* compounds as shown by the intense absorption at about 975 cm^{-1} and no strong or medium absorption from 900 to 680 cm^{-1} . The specificity of the reaction is shown by the fact that 2-methylcyclohexanone gives none of the 6-heptenal although the methyl group is also β to the carbonyl group; 2-ethylcyclopentanone gives only 4-heptenal and no 5-heptenal while 2-*n*-propylcyclopentanone gives only 4-octenal and no 5-octenal. These observations on the five-membered cyclic ketones have made arguments concerning the role of axial and equatorial protons in this reaction (in six-membered cyclic ketones) superfluous. Lastly, the self-quenching of reaction 2 by the aldehyde that is formed seems strong in terminally unsaturated aldehydes but less so in other unsaturated aldehydes. The existence of this effect explains the failure to obtain substantial yields of the aldehyde by reaction 2 in preparative scale photolysis.

Acknowledgments. The authors wish to thank Drs. E. B. Whipple, D. Arnold, and R. L. Hinman of the Union Carbide Research Center, Tarrytown, N. Y., for the n.m.r. spectra.

(19) S. E. Cremer and R. Srinivasan, unpublished results.

An Electron Spin Resonance Study of the Anion Radicals of 9,10-Diazaphenanthrene, 2,2'-Bipyrimidine, and $\Delta^{2,2'}$ -Biisobenzimidazolylidene

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Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. Received December 3, 1964

Electron spin resonance spectra were obtained for the anion radicals of 9,10-diazaphenanthrene, 2,2'-bipyrimidine, and $\Delta^{2,2'}$ -biisobenzimidazolylidene in dimethylformamide solution. Polarographic data were obtained for reduction of the neutral polyazines as well as for related hydrocarbons. The ^{14}N coupling constant for the 9,10-diazaphenanthrene anion is 5.27 ± 0.04 gauss (two equivalent nuclei with $I = 1$); four proton coupling constants, each corresponding to two equivalent protons, have the values 3.58 ± 0.03 , 2.83 ± 0.03 , 0.77 ± 0.01 , and 0.283 ± 0.003 gauss. The ^{14}N coupling constant in the anion radical of 2,2'-bipyrimidine is 1.405 ± 0.03 gauss and the two proton coupling constants are 4.98 ± 0.04 (two equivalent protons) and 0.145 ± 0.01 gauss (four equivalent protons). For the anion radical of $\Delta^{2,2'}$ -biisobenzimidazolylidene the nitrogen coupling constant is 2.97 gauss and the two proton cou-

pling constants (each corresponding to four equivalent protons) are 1.40 and 0.83 gauss. The ^{14}N coupling constants are discussed in relation to values reported for other azine anion radicals.

Introduction

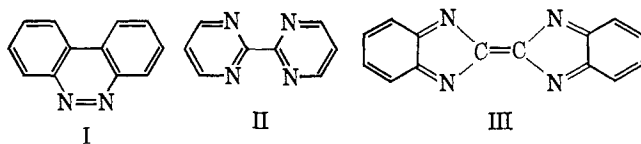
The catalog of azine anion radicals studied by electron spin resonance (e.s.r.) spectroscopy has grown rapidly over the past 3 years. The anion radical of 4,4'-bipyridine was examined in 1961 by Ward¹ and subsequently by Carrington and Santos-Veiga.² E.s.r. studies have also been done on the anion radicals of 2,2'-

(1) R. L. Ward, *J. Am. Chem. Soc.*, **83**, 3623 (1961).

(2) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

bipyridine,^{3,4} pyrazine,^{2,5-9} 2,5-dimethylpyrazine,¹⁰ 2,6-dimethylpyrazine,¹⁰ pyridazine,^{6,10} quinoxaline,^{2,6} phenazine,^{2,6,9,11} 1,4,5,8-tetraazaanthracene,² s-tetrazine,⁹ phthalazine,⁹ and 1,3,6,8-tetraazapyrene.¹² The anion radicals of 3,5-lutidine⁸ and cycl[3.2.2]azine¹³ are the only monoazine anion radicals which have been examined.

Of primary interest in the e.s.r. study of azine anion radicals has been the evaluation of isotropic nitrogen and hydrogen coupling constants. Rationalization of these coupling constants in terms of π -electron spin densities continues to be a significant concern in the study of the electronic structure of organic radicals. We wish to report the e.s.r. spectra of the anion radicals of three polyazines: 9,10-diazaphenanthrene (I), 2,2'-bipyrimidine (II), and $\Delta^{2,2'}$ -biisobenzimidazolydene (III).



Experimental

Dimethylformamide secured as Eastman Spectrograde was purified by storage over potassium carbonate followed by distillation at reduced pressure. 9,10-Diazaphenanthrene was used as received from Aldrich Chemical Co. A sample of the recently synthesized¹⁴ 2,2'-bipyrimidine was kindly supplied to us by Professor M. G. Mellon, Purdue University. We are grateful to Dr. J. H. M. Hill, Hobart and William Smith Colleges, for the sample of $\Delta^{2,2'}$ -biisobenzimidazolydene as prepared by the oxidation of benzimidazole.¹⁵

Anion radicals were generated electrochemically in dimethylformamide solution using the *intra muros*¹⁶ and recirculation techniques¹⁷ described earlier. E.s.r. spectra were obtained using a Varian V-4502 spectrometer with 100-kc. field modulation in conjunction with a Varian 12-in. magnet. Field calibration markers were placed directly on recorded spectra as described previously.¹⁸ Computation of theoretical e.s.r. spectra was done using the computer program of Stone and Maki¹⁹

Polarographic data were secured at 25.0° using a dropping mercury electrode together with the ORNL three-electrode polarograph (Indiana Instruments, Bloomington, Ind.). An aqueous saturated calomel reference electrode was employed. Diffusion current constants, $i_d/m^{2/3}t^{1/6}C$, refer to maximum, not average, currents.

Results

Polarographic data as obtained for the reduction of the azines and related hydrocarbons are presented in Table I. It is notable that the azines are more readily reduced than the corresponding aromatic hydrocarbons.

Table I. Polarographic Data^a

	$E_{1/2}$, v. vs. s.c.e.	$-(E_{3/4} - E_{1/4})$, mv.	i_d/f , $m^{2/3}t^{1/6}C^b$
9,10-Diazaphenanthrene	-1.482	79	2.9
Phenanthrene	-2.425	68	3.0
2,2'-Bipyrimidine	-1.766	59	2.9
Biphenyl	-2.60	73	3.6
$\Delta^{2,2'}$ -Biisobenzimidazolydene	-0.313	59	2.2

^a Dimethylformamide solution, 0.1 M tetraethylammonium perchlorate as supporting electrolyte. ^b Dimensions are $\mu\text{a. mg.}^{-2/3} \text{sec.}^{1/2} \text{mM}^{-1}$.

The e.s.r. spectrum of the anion radical of 9,10-diazaphenanthrene is shown in Figure 1a. Three spectra were measured in the assignment of a ¹⁴N coupling constant of 5.27 ± 0.04 gauss (two equivalent nuclei with $I = 1$) and four proton coupling constants, each corresponding to two equivalent nuclei of spin $1/2$, with the values 3.58 ± 0.03 , 2.83 ± 0.03 , 0.77 ± 0.01 , and 0.283 ± 0.003 gauss. Uncertainties are expressed here as standard deviations. A calculated spectrum using the above coupling constants and a line width of 0.14 gauss is given in Figure 1b.

The 2,2'-bipyrimidine anion was obtained by electroreduction of approximately millimolar solutions of the neutral compound. Such solutions were circulated through the microwave cavity.¹⁷ From e.s.r. spectra such as that shown in Figure 2a the following coupling constants (in gauss) were assigned: $a^N = 1.405 \pm 0.03$ (four equivalent nitrogens), $a^H = 4.98 \pm 0.04$ (two equivalent hydrogens), $a^H = 0.145 \pm 0.01$ (four equivalent hydrogens). The calculated spectrum is shown in Figure 2b.

The electron spin resonance spectrum of the anion radical of III is shown in Figure 3a. The assigned coupling constants are $a^N = 2.97$, $a^H = 1.40$, and $a^H = 0.83$ gauss, all for four equivalent nuclei. A calculated spectrum using these coupling constants and a line width of 0.090 gauss is given as Figure 3b.

Discussion

9,10-Diazaphenanthrene Anion. It is appropriate to consider the coupling constants for the anion radical of 9,10-diazaphenanthrene in relation to the coupling constants for the anion radical of the related hydrocarbon, phenanthrene. For this purpose the proton coupling constants for the phenanthrene anion radical in acetonitrile solution²⁰ are shown in Figure 4a. The

(20) S. H. Glarum and L. C. Snyder, *ibid.*, 36, 2989 (1962).

(3) A. Zahlan, F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, 37, 683 (1962).

(4) W. L. Reynolds, *J. Phys. Chem.*, 67, 2866 (1963).

(5) J. C. M. Henning and C. de Waard, *J. Chem. Phys.*, 35, 2258 (1961).

(6) R. L. Ward, *J. Am. Chem. Soc.*, 84, 332 (1962).

(7) C. A. McDowell, K. F. Paulus, and J. R. Rowlands, *Proc. Chem. Soc.*, 60 (1962).

(8) N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, 5, 509 (1962).

(9) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 39, 1635 (1963).

(10) C. A. McDowell and K. F. G. Paulus, *Mol. Phys.*, 7, 541 (1964).

(11) K. H. Hauser, A. Habich, and V. Franzen, *Z. Naturforsch.*, 16a, 836 (1961).

(12) F. Gerson, *Helv. Chim. Acta*, 47, 1484 (1964).

(13) N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, 6, 265 (1963); F. Gerson and J. D. W. van Voorst, *Helv. Chim. Acta*, 46, 2257 (1963).

(14) D. D. Bly and M. G. Mellon, *J. Org. Chem.*, 27, 2945 (1962).

(15) J. H. M. Hill, *ibid.*, 28, 1931 (1963).

(16) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, 82, 2671 (1960).

(17) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 39, 778 (1963).

(18) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, 86, 987 (1964).

(19) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 38, 1999 (1963).

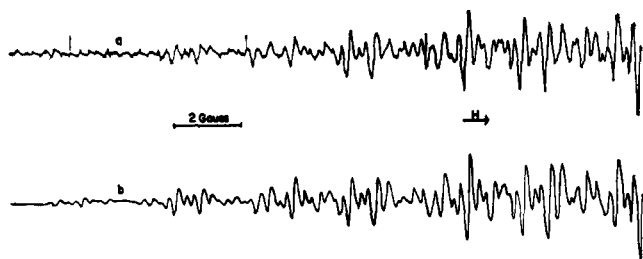


Figure 1. (a) Derivative e.s.r. spectrum of anion radical of 9,10-diazaphenanthrene from electroreduction of 0.5 mM dimethylformamide solution of parent compound (only the low-field half of spectrum is shown). (b) Calculated spectrum obtained using coupling constants given in text and line width of 0.14 gauss and a Lorentzian line shape.

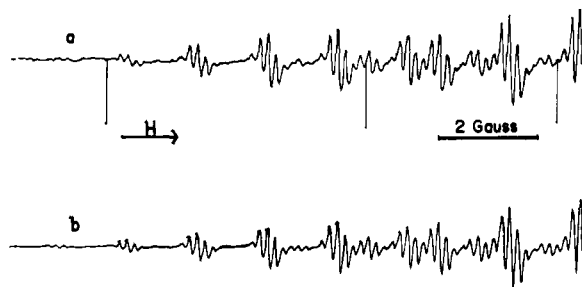


Figure 2. (a) Derivative e.s.r. spectrum of anion radical of 2,2'-bipyrimidine from electroreduction of ca. 1 mM dimethylformamide solution of parent compound (only the low-field half of spectrum is shown). (b) Calculated spectrum obtained using coupling constants given in text and line width of 0.07 gauss and a Lorentzian line shape.

assignment of coupling constants to particular molecular positions is based on spin density calculations of McLachlan²¹ and has not been verified in detail by specific deuteration. However, Glarum and Snyder²⁰ have presented experimental evidence supporting assignment of the smallest proton coupling constant to the position shown in Figure 4a.

Table II. HMO Calculation of Spin Densities for 9,10-Diazaphenanthrene and Phenanthrene Anions

Molecular position ^a	A ^b	B ^c	C ^d
1	0.265	0.220	0.172
2	7×10^{-6}	0.011	...
3	0.083	0.082	0.116
4	0.007	0.015	0.002
5	0.070	0.077	0.099
6	0.024	0.021	0.054
7	0.050	0.072	...

^a Numbering as given in Figure 4. ^b Calculation done setting $\alpha_N = \alpha_C + 0.75\beta_{CC}$. ^c Calculation done setting $\alpha_N = \alpha_C + 1.2\beta_{CC}$ and $\beta_{CN} = 1.2\beta_{CC}$. ^d Values for phenanthrene anion as quoted by T. C. Sayetta and J. D. Memory, *J. Chem. Phys.*, **40**, 2748 (1964).

As an *a priori* aid to establishing the correct assignment of proton coupling constants in the 9,10-diazaphenanthrene anion a Hückel molecular orbital (HMO) calculation of spin densities was performed. The usual procedure of increasing the value of the Coulomb integral for the nitrogen atom as compared to the carbon

(21) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

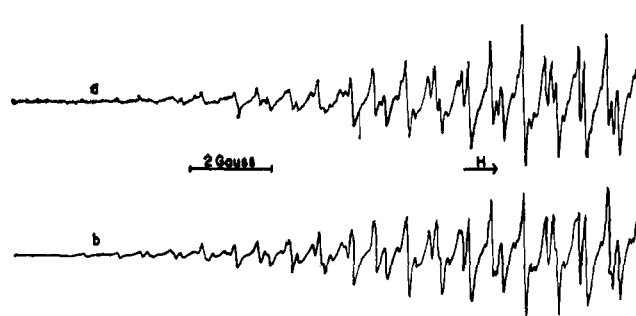


Figure 3. (a) Derivative e.s.r. spectra of anion radical of $\Delta^{2,2'}$ -biisobenzimidazolyliene obtained by electroreduction of 0.45 mM dimethylformamide solution of parent compound (only the low-field half of spectrum is shown). (b) Calculated spectrum using coupling constants given in text and line width of 0.09 gauss and a Lorentzian line shape.

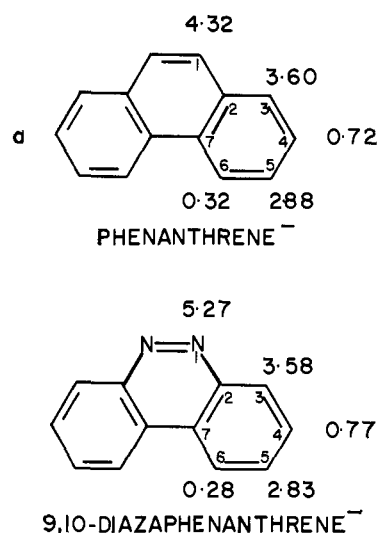


Figure 4. Assignment of coupling constants in gauss to molecular positions in the phenanthrene and 9,10-diazaphenanthrene anion radicals.

atom was followed. All resonance integrals were set equal to β_{CC} unless otherwise indicated. The results of calculations for two different choices of Coulomb integrals along with the HMO values for phenanthrene anion are given in Table II. These calculations indicate that the spin density distribution in 9,10-diazaphenanthrene is not expected to be grossly different from that in the phenanthrene anion; thus we have assigned coupling constants as shown in Figure 4b following the pattern for phenanthrene anion. It is possible that the coupling constants at positions 4 and 6 should be interchanged, but it seems less likely this is the case for positions 3 and 5. Comparable ring proton coupling constants in the anion-radical pairs anthracene-phenazine and naphthalene-phthalazine do not show the same close similarity as is noted here for the phenanthrene and 9,10-diazaphenanthrene anion radicals.

Stone and Maki⁹ have discussed the relationship between spin densities and ¹⁴N coupling constants in azine anions on the basis of the Karplus-Fraenkel²² treatment of ¹³C coupling constants. For an *o*-diazine anion such as the 9,10-diazaphenanthrene

(22) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

anion, the expression suggested by Stone and Maki⁹ for the ¹⁴N coupling constant is

$$a^N = (S^N + Q_{NC}^N)\rho^N + Q_{CN}^N\rho_2^C \quad (1)$$

where S^N and Q_{NC}^N are the spin polarization parameters for the nitrogen 1s and 2s electrons, respectively. It is likely that the $Q_{CN}^N\rho_2^C$ term²³ in eq. 1 is small by comparison with the remaining contributions to the nitrogen coupling constant in the 9,10-diazaphenanthrene anion since Q_{CN}^N has been estimated⁹ as -2 ; furthermore, data in Table II suggest that $\rho_2^C < 0.02$. Stone and Maki⁹ have estimated the value of $(S^N + Q_{NC}^N)$ as 21.1 gauss. Using this value in eq. 1 with the experimental nitrogen coupling constant of 5.27 gauss yields a nitrogen spin density of 0.25 which does fall within the range of calculated values in Table II.

An alternative estimate for the nitrogen spin density is available by using the relation between ring proton coupling constants, a^H , and spin density on the contiguous carbon atom, ρ^C , as stated in eq. 2.²⁴ Assuming

$$a^H = Q_{CH}^H\rho^C \quad (2)$$

that the spin densities at carbon atoms 3, 5, and 6 are positive and letting $Q_{CH}^H = -24$ gauss we estimate that the total spin density at the six carbon atoms at positions 3, 5, and 6 is 0.558.²⁵ By analogy to the

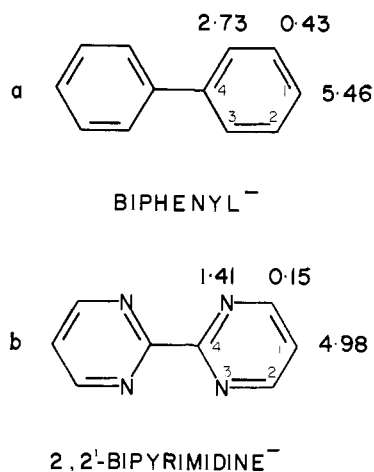


Figure 5. Assignment of coupling constants in gauss to molecular positions in the biphenyl and 2,2'-bipyrimidine anion radicals.

phenanthrene anion²¹ we regard the spin density at position 4 as negative and thus the total spin density available for distribution at the nitrogen atoms and carbon atoms 2 and 7 is 0.507. Thus the nitrogen spin density is given by eq. 3. Since carbon 2 is situated

$$\rho^N = 0.254 - (\rho_7^C + \rho_2^C) \quad (3)$$

between atoms of fairly large positive spin densities, the possibility exists that ρ_2^C is negative.²⁶ Thus while the

(23) The notation ρ_i^C indicates spin density on the carbon atom at the i th position (see Figures 4 and 5).

(24) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(25) This estimate is necessarily dependent on the value assigned to Q_{CH}^H . Thus if Q_{CH}^H is taken to be 28 gauss, instead of 24 gauss, the spin density on positions 3, 5, and 6 is 0.48. Furthermore, we have not included the second-order dependence of a^H on charge density at the contiguous carbon atom as discussed by J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963), and T. C. Sayetta and J. D. Memory, *J. Chem. Phys.*, **40**, 2748 (1964).

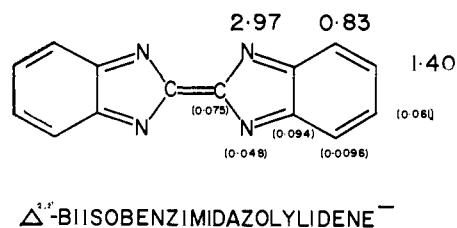


Figure 6. Coupling constants in gauss for anion radical of $\Delta^{2,2'}$ -bisobenzimidazolylidene given in upper part of figure and calculated spin densities given in lower part.

sum $(\rho_7^C + \rho_2^C)$ in eq. 3 could be a small negative number, it is more likely that it is a small positive number since ρ_7^C is estimated as 0.05–0.07 in Table II. We conclude that ρ^N estimated from consideration of proton coupling constants and conservation of spin is reasonably consistent with the Stone and Maki estimate of $(S^N + Q_{NC}^N)$.

2,2'-Bipyrimidine Anion. Coupling constants for the 2,2'-bipyrimidine anion can be assigned unequivocally to the molecular positions shown in Figure 5b. For purposes of comparison the coupling constants² for the biphenyl anion are shown in Figure 5a. The implications are that replacement of the CH fragment at position 3 by a nitrogen atom results in some withdrawal of spin density from ring positions 1 and 2 and an increase at positions 3 and/or 4.

The expression⁹ analogous to eq. 1 which is applicable to the nitrogen coupling constant in the 2,2'-bipyrimidine anion is given in eq. 4. HMO calculations of

$$a^N = (S^N + 2Q_{NC}^N)\rho^N + Q_{CN}^N(\rho_4^C + \rho_2^C) \quad (4)$$

spin densities as presented in Table III provide a *primitive* indication that a significant spin density does reside at a position adjacent (position 4) to the nitrogen atom. Thus in principle the nitrogen coupling constant in the 2,2'-bipyrimidine anion should offer a test of the significance of the Q_{CN}^N term in eq. 4.

Table III. HMO Calculation of Spin Densities for 2,2'-Bipyrimidine Anion

Molecular position ^a	A ^b	B ^c	C ^d
1	0.114	0.132	0.130
2	0.005	0.006	0.009
3	0.094	0.074	0.067
4	0.187	0.206	0.218

^a See Figure 5 for numbering. ^b $\alpha_N = \alpha_C + 0.75\beta_{CC}$. ^c $\alpha_N = \alpha_C + 1.2\beta_{CC}$; $\beta_{CN} = 1.2\beta_{CC}$. ^d Coulomb and resonance integrals are the same as for column B except the resonance integral between bridge carbon atoms is set equal to $0.8\beta_{CC}$.

Unfortunately, a rigorous test is not possible since we do not know if the anion radical is planar. A qualitative indication of the change of spin densities as the two rings are twisted with respect to each other is afforded by examination of columns B and C in Table III. Decreasing the resonance integral between the bridge carbon atoms from β_{CC} to $0.8\beta_{CC}$ to simulate twisting the two rings increases the spin density at ring position 4 and decreases spin density at the nitrogen

(26) However, the comparable position in the phenanthrene anion possesses a positive spin density.²¹

atoms. The calculations in Table III are clearly imperfect since predicted values of ρ_1^C are all low by comparison with the experimental proton coupling constant of 5.0 gauss which corresponds to $\rho_1^C \approx 0.2$. Nevertheless, we note with interest that if the spin densities in column B, Table III, are used together with the Stone-Maki⁹ estimate of $(S^N + 2Q_{NC}^N)$, 30.9 gauss, then the magnitude of the experimental nitrogen coupling constant can be reproduced by choosing Q_{CN}^N as -4.1 gauss.

$\Delta^{2,2'}$ -Biisobenzimidazolylidene Anion. For the first two azine anions discussed, it was possible to examine the coupling constants of the analogous hydrocarbon anion radicals. That is not the case for the anion of compound III since the corresponding hydrocarbon, 2,2'-biisoidene, has not been synthesized.

Results of a HMO calculation of spin densities in the $\Delta^{2,2'}$ -biisobenzimidazolylidene anion are shown in Figure 6.²⁷ The experimental proton coupling con-

stants were assigned to the molecular positions shown in Figure 6 solely on the basis of the HMO calculations. The close agreement between the larger proton coupling constant, 1.40 gauss, and the value of 1.46 gauss which is predicted from eq. 2 and the calculated spin density (Figure 6) must be regarded as fortuitous.

Because the interior CNC angle in this anion radical is expected to be somewhat smaller than the angle of ca. 120° in the benzenoid azine radicals, the spin polarization parameters in eq. 4 will be changed. Thus a direct comparison of the nitrogen coupling constant in the anion radical of III with other nitrogen coupling constants is not possible.

Acknowledgments. This work was supported by the National Science Foundation through Grant NSF-GP-1985. Partial support for purchase of the e.s.r. spectrometer through National Science Foundation Grant GP-1687 is gratefully acknowledged.

(27) Calculation done with $\alpha_N = \alpha_C + 0.75\beta_{CC}$.

Computation of Association Constants from Spectrophotometric Data. II. Multiple Equilibria

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Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas. Received December 8, 1964

It is shown that the criterion of linearity of Benesi-Hildebrand plots for indicating the presence of only stable 1:1 charge-transfer complexes and/or "contact" absorptions is not a valid one. Synthetic data were calculated for systems involving the formation of stable AD and A₂D, and also AD and AD₂ charge-transfer complexes. Widely different values of K₁, K₂, and of the molar absorptivities of the complexes were used in calculating these data. In no case, however, did the resulting Benesi-Hildebrand plots reveal significant variations from linearity such that the presence of the second stable charge-transfer complex would be suspected. It was found that the Benesi-Hildebrand method gave values of K which exhibited a systematic variation with wave length. The system tetracyanoethylene-naphthalene-carbon tetrachloride was carefully examined, and a systematic variation of K with wave length was observed. The results cannot be explained by isomeric, stable 1:1 charge-transfer complexes and/or "contact" absorptions. It is necessary to postulate the existence of stable charge-transfer complexes of at least two different stoichiometries. Temperature dependencies of ΔH and total oscillator strengths can yield no useful information for such systems. The present work indicates the necessity to examine the variation of K with wave length in order to pass upon

the presence or absence of equilibria other than 1:1 stable isomeric charge-transfer complexes and/or "contact" absorptions.

Spectrophotometric methods have been employed in the determination of a great variety of association constants. These constants have been determined by graphical procedures. A relationship between absorbances and association constants was first reported by Benesi and Hildebrand.² If an initial concentration of an acceptor molecule, [A₀], is mixed in an inert solvent with a donor molecule of original concentration [D₀], an interaction occurs to form a charge-transfer complex: A + D ⇌ C. The equilibrium constant for this association is given by

$$K = \frac{C}{(A_0 - C)(D_0 - C)} \quad (1)$$

where italic letters A, C, and D refer to concentrations of A, C, and D. The absorbance is given by application of the Beer-Lambert law

$$\text{O.D.}/b = \epsilon_a(A_0 - C) + \epsilon_d(D_0 - C) + \epsilon_c C \quad (2)$$

where O.D. = optical density (absorbance), b = path length in cm., and ϵ_i = molar absorptivities.

(1) (a) Portion of a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry at Kansas State University; (b) National Science Foundation Research Participation for College Teachers Fellow.

(2) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949).