Carbon-13 Magnetic Resonance. XIV.[1] Aza-Analogs of Polycyclic Aromatic Hydrocarbons

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Abstract: The carbon-13 chemical shifts for naphthalene and anthracene along with some of their mono and diaza analogs are reported. Additive relationships between structural features and these chemical shift values were found, and these provide a highly reliable method for making spectral assignments. Quantum mechanical treatments of the chemical shift data were used to rationalize shift values in terms of the paramagnetic screening mechanisms. Using EHT and CNDO wave functions, these calculations characterized certain types of weaknesses in these approximate treatments, and some modifications were suggested for improving the wave functions. It is concluded that inductive and resonance effects expected for this class of compounds are adequate to account for the principle variations noted in the carbon-13 chemical shift data. Furthermore, the agreement supports the position that the simple wave functions for these relatively large molecules are faithfully accounting for the essential features of the electronic structure.

The work of Alger, Grant, and Paul[2] demonstrated the feasibility of investigating the electronic structure of polycyclic aromatic hydrocarbons by means of carbon-13 magnetic resonance. Even though the chemical shifts at the bridgehead carbons proved difficult to rationalize theoretically, these authors outlined the importance of both charge density and bond-order terms in discussing the magnetic shielding of the carbon-13 nucleus.

Using the extended Huckel theory,[3] Adam, *et al.*,[4] have discussed the relationship between total charge density and the proton and carbon-13 chemical shifts observed in quinoline, isoquinoline, and a number of five- and six-membered heterocycles. Bloor and Breen[5] have calculated the carbon-13 chemical shifts of these same compounds using the magnetic shielding expression of Karplus and Pople[6] and the valence-shell SCF–MO–CNDO/2 (Complete Neglect of Differential Overlap) of Pople, *et al.*[7–9] The calculations of Bloor and Breen indicate that the correlation between carbon-13 chemical shifts and total electronic charge is an improvement over the results obtained by considering π charge densities alone.

In the present work the extended Hückel theory, as well as the CNDO/2 method, are used to provide wave functions from which the chemical shifts are calculated according to the formalism used previously by the authors.[10] The chemical shift data for anthracene is given for the first time and the shift values of naphthalene and anthracene are considered as a basis for discussing the aza-analogs of these compounds. The aza-analogs of the alternate aromatic hydrocarbons provide a much wider range of chemical-shift values on which to base theoretical considerations than is present in the parent carbocyclic species.[11]

The proton spectra of several of the heterocyclic species are seriously complicated by overlapping of the spectral multiplets. For example, the proton spectra of quinoline is an ABX spectral type in the hetero ring and an ABCD spectra in the benzenoid ring. Several partial interpretations[12–16] preceded the complete analysis by Black and Heffernan.[17] These authors have also obtained complete analyses for the proton spectra of isoquinoline[18] and the diazanaphthalenes.[19] The chemical shifts reported in ref 19 were modified in the case of quinazoline in accordance with the work of Katritzky, *et al.*,[20] while the proton shifts reported for acridine[21] and phenazine[22] were used as a basis for interpreting the carbon-13 spectra of concentrated solutions of these compounds. The proton chemical shifts of anthracene have been investigated by several workers[23–25] and the values reported by Martin, *et al.*,[25] are used in this study.

A comparison of the carbon-13 chemical shifts in naphthalene with those found in quinoline and isoquinoline provides additivity parameters which prove useful in making peak assignments in the diazanaph-

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thalenes. These parameters are used in those cases where proton chemical shift assignments are obscure.

Experimental Section

A. **Equipment.** The analog frequency sweep spectrometer (Varian AFS-60) used in this work derives its 15 MHz frequency from a Hewlett Packard G 103A frequency synthesizer controlled by a Varian V-4313 analog programmer. The probe is double tuned to 15 and 60 MHz with the 60 MHz component used to provide field-frequency stabilization. The field may be locked by conventional techniques to either a proton resonance in the sample or to an external water sample mounted behind the sample insert. The external lock mode is utilized whenever proton decoupling is required. Proton decoupling is accomplished using a Hewlett Packard 5102A frequency synthesizer operating at 30-31 MHz equipped with a Hewlett Packard 10515A doubler. The stable 60 MHz frequency thus generated is amplified by a Varian V-4320 spin decoupler and introduced to the same through the internal lock circuit. The advantages of proton decoupling techniques (multiplet collapse and a nuclear Overhauser effect) are realized in improving the signal-to-noise ratio. Further improvement of the signal height is realized by employing the Varian C-1024 time averaging device.

B. **Experimental Technique.** Chemical shifts were determined by decoupling one of the isolated resonance peaks in each sample and using the method described by Paul and Grant[26] to calculate the chemical shift value relative to benzene. Once the chemical shift value of this fiducial mark has been determined, all other peaks in the sample are decoupled and their shift values can be measured directly from their corresponding 15 MHz resonance frequencies. By using a high decoupler power, a frequency setting midway within the range of the sample protons will usually suffice to decouple most of the carbon peaks observed in a single spectral scan. If low decoupler power is used, however, the decoupler may be set on each individual proton frequency to provide selective decoupling. Under these conditions only the directly bonded carbon atom exhibits the characteristic decoupled singlet. By stepping the decoupler frequency at reduced power through the known resonance positions of the proton spectrum, the carbon-13 peaks can be associated with their directly bonded protons and the chemical shift assignments made with relative ease. Whenever there is considerable overlapping of the proton spectra and the shifts are separated by only a few cps, the assignment of the carbon resonance peaks cannot be made with complete certainty by this "selective decoupling" technique. In these cases unequivocal peak assignments were made by observing the spectra of deuterium labeled compounds. Since bridgehead carbons are relatively insensitive to decoupler frequency[27] the corresponding peaks are readily recognized.

C. **Sample Preparation.** With the exceptions of 5- and 7-deuterioquinoline, all species investigated were obtained from standard commercial sources. Quinoline, the deuterioquinolines, and isoquinoline were run as neat liquids. Anthracene was observed in a saturated benzene solution and all other species were studied in saturated chloroform solutions.

7-Deuterioquinoline. To a solution of 10.4 g (0.05 mol) of 7-bromoquinoline[28] in 150 ml of ethanol water (1:1) was added 4.2 g (0.05 mol) of sodium hydrogen carbonate and 2 g of 5% palladium on charcoal catalyst. This mixture was shaken for 4 hr on a Parr hydrogenator under 16 psi deuterium gas. The resulting mixture was filtered and the filtrate was concentrated under reduced pressure to a small volume. Ether (50 ml) and water (25 ml) were added and the phases were separated. The aqueous phase was extracted with an additional two 50 ml portions of ether and the combined organic layer was washed with 25 ml of water and dried over sodium sulfate. This mixture was filtered and the filtrate was evaporated to a yellow oil under reduced pressure. The oil was dissolved in 5 ml of chloroform and this solution was applied to a dry-packed column (1 × 36 in. (200 g)) of silica gel.[29] After drying for 15 hr the column was developed using chloroform acetone (97:3); 30 ml fractions were collected. Fractions 5–8 contained a bright yellow impurity, 9–11 contained this material and 7-deuterioquinoline, 12–28 contained only 7-deuterioquinoline as judged by thin layer chromatography, boiling point, and uv spectral identity with quinoline. Fractions 12–28 were pooled and evaporated under reduced pressure to yield 4.3 g (66%) of pure 7-deuterioquinoline. This product had ^1H and ^{13}C nmr spectra identical with those of quinoline except for the absence of absorption and splitting due to 7-D substitution.

5-Deuterioquinoline. Catalytic reduction of 5-bromoquinoline[28] was effected with deuterium gas exactly as with 7-bromoquinoline.

Results

A. **Quinoline and Isoquinoline.** Table I contains the carbon-13 chemical-shift data for quinoline and isoquinoline, along with the peak assignments. These two compounds have no symmetry features and therefore the decoupled spectrum in each case consists of 9-unit intensity lines which cannot be assigned on the basis of peak height. Except for the bridgehead carbons in both compounds and for C-5 and C-7 in quinoline, selective decoupling methods, however, could be used to make the spectral assignments from known proton shifts. The proton shifts at position 5 and 7 in quinoline were too close together to allow a distinction to be made on the basis of proton decoupling data. Elimination of large proton splittings in the carbon-13 spectra of the 5 and 7 deuterated quinolines resolved this ambiguity and the assignments resulting from study of these two samples are given in Table I.

Bridgehead assignments in both quinoline and isoquinoline were made on the strength of shift values found in pyridine (*i.e.*, α, −21.72; β, +4.54; and γ, −7.42). In quinoline the effect of the nitrogen atom reflects the α and β pyridine shifts as the bridgehead carbons have respective shift values of −20.5 and −0.20 ppm. Likewise, the −0.59 and −7.49 ppm bridgehead shifts in isoquinoline may be characterized with β and γ nitrogen parameters, respectively. In both of these compounds the β shifts are about 5 ppm to lower field than the corresponding β shift in pyridine. This may be rationalized, however, on the basis of the −5.20 ppm bridgehead shift found for naphthalene which is also included in Table I for convenience in making comparisons with the related aza-analogs. A similar −5 ppm shift relative to pyridine was not observed at bridgehead carbons α and γ to the nitrogen atom in quinoline and isoquinoline, respectively, and therefore it is really these bridgehead carbons which are reflecting a nonadditive feature. The peripheral carbons in the hetero ring also exhibit pyridine-type shifts as shown by the remaining chemical shifts for the hetero ring in quinoline which are $\alpha = -22.36$, $\beta = +6.95$ and $\gamma = 7.54$ ppm, while the values in isoquinoline are $\alpha = -15.29$ and -24.62 and $\beta = +7.68$. The marked similarity in shift values between pyridine and these bicyclic systems is readily apparent, and it is clear that a nitrogen atom has characteristic effects upon a six-membered aromatic ring, even though it may be a part of a polycyclic system. While the benzenoid ring system interacts with the hetero ring to produce interesting variation in the chemical shifts (*e.g.*, the two carbons α to the nitrogen in isoquinoline are separated by 9.33 ppm), even so the primary effect of the nitrogen atom dominates these secondary effects and the peaks are found to occur in characteristic spectral regions. It is anticipated that this feature will continue to be ex-

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Table I. Carbon-13 Chemical Shifts in Naphthalene, Anthracene, and Selected Nitrogen Heterocyclic Derivatives

Item no.	Compound	Position	δ_{H}[a], ppm	$\delta_{\mathrm{C}^{13}}$[a], ppm
1	Naphthalene[e]	1,4,5,8		+0.44
2		2,3,6,7		+2.56
3		9,10		−5.20
4	Quinoline	2	−1.86	−22.36
5		3	+0.07	+6.95
6		4	−0.66	−7.54
7		5	−0.41	+0.16
8		6	−0.18	+1.69
9		7	−0.43	−1.24
10		8	−1.26	−1.59
11		9		−20.51
12		10		−0.20
13	Isoquinoline	1	−2.28	−24.62
14		3	−1.60	−15.29
15		4	−0.32	+7.68
16		5	−0.40	+1.69
17		6	−0.29	−1.99
18		7	−0.20	+0.97
19		8	−0.57	+0.64
20		9		−0.59
21		10		−7.49
22	Quinoxaline	2,3	−1.58	−16.98
23		5,8	−0.91	−1.31
24		6,7	−0.30	−1.41
25		9,10		−14.69
26	Phthalazine	1,4	−2.51	−23.52
27		5,8[b]	−0.86	+1.84
28		6,7[b]	−0.86	−4.68
29		9,10		+1.84
30	Cinnoline	3	−2.83	−17.62
31		4	−1.40	+3.87
32		5[b]	−1.0 ± 0.1[d]	+0.59
33		6	−0.93	−3.78
34		7[b]	−1.0 ± 0.1[d]	−3.62
35		8	−1.73	−1.02
36		9		−22.51
37		10		+1.68
38	Quinazoline	2	−2.22	−31.99
39		4	−2.29	−27.20
40		5[b]	−0.6 ± 0.1[d]	+1.10
41		6	−0.31	+0.57
42		7[b]	−0.6 ± 0.1[d]	−5.63
43		8	−0.83	−0.06
44		9		−21.63
45		10		+3.29
46	Anthracene[c]	1,4,5,8		−1.60
47		2,3,7,6		+2.98
48		9,10		−4.06
49		11,12,13,14		−3.74
50	Acridine	1,8	−0.96	−1.03
51		2,7	−0.39	+0.17
52		3,6	+0.02	+3.03
53		4,5	−0.45	−1.81
54		10	−1.10	−7.39
55		11,14		+1.96
56		12,13		−20.64
57	Phenazine	1,4,5,8	−0.91	−2.42
58		2,3,6,7	−0.29	−1.78
59		11,12,13,14		−15.50

[a] Values given with respect to benzene. [b] Assignments made from parameters given in Table II. [c] Proton spectra were masked by the large peak due to benzene which was used as solvent. The proton shift values were obtained from ref 25. [d] The spectra were too complex at 60 MHz and high concentration to resolve H-5 and H-7. [e] Values taken from ref 2.

ploited in the identification of quinoline and isoquinoline derivatives.

B. Diazanaphthalenes. The chemical-shift data and spectral assignments for the diazanaphthalenes are also contained in Table I. Both bridgehead carbons in quinoxaline and in phthalazine have identical shifts in their respective compounds because of molecular symmetry and may be easily recognized by the absence of large proton-induced splittings. It is well to note that the shift of C-9,10 in phthalazine is accidentally degenerate with the C-5,8 carbon and the two decoupled singlets are not resolvable. Even so, this creates no difficulty in making assignments as the spectral features are easily characterized in the regular coupled spectrum where the C-5,8 carbons exhibit a large doublet splitting while no such coupling is found at C-9,10. There is, therefore, no ambiguity in the assignment of one of these singlet peaks to the bridgehead carbons. The bridgehead carbons in cinnoline and quinazoline are again distinguishable from other carbon peaks because of the absence of large proton splittings. Having designated the two bridgehead peaks in each case, final differentiation rests on the large negative shift noted in those carbons α to a nitrogen atom. In both of these cases one bridgehead (α to one of the nitrogens) appears below −20 ppm and the other above +1.0 ppm. It is felt that this large separation provides adequate assurance that the assignments given in Table I are correct for bridgehead carbons.

All six of the remaining carbons in the hetero ring and six of the twelve peripheral benzenoid carbons in the diazanaphthalenes were assigned from known proton shifts using the selective decoupling technique. The remaining benzenoid carbons (C-5,8 and C-6,7 in phthalazine, C-5 and C-7 in cinnoline, and C-5 and C-7 in quinazoline), however, could not be assigned from decoupling data due to ambiguities in the corresponding proton shifts for the magnetic field being used and the concentrations required to obtain carbon-13 spectra. Attention was then directed toward the discovery of possible additive structural parameters to remove the remaining ambiguities existing in the three pairs of carbon shifts (items 27, 28, 32, 34 and 40, and 42 in Table I). It is to be noted that these shifts can be predicted with reasonable accuracy from nitrogen positional parameters obtained by subtracting from the quinoline and isoquinoline chemical shifts the corresponding value for each position in naphthalene. The particular set of substituent parameters obtained in this way are given in column I of Table II. Working in reverse, these parameters are then used to predict shifts for the six unassigned carbons in the diazanaphthalenes and the

Table II. Benzenoid Ring Substituent Parameters

Type of nitrogen structure (*i* value)	Carbon position affected (*j* value)	Substituent parameters, δ_{ij}	Parametric values[a] I	Parametric values[a] II
Quinoline type	8	δ_8	−2.03	−1.73
($i = 1$)	7	δ_7	−3.80	−3.64
	6	δ_6	−0.87	−0.65
	5	δ_5	−0.28	−0.27
Isoquinoline type	8	δ_{28}	+0.20	+0.45
($i = 2$)	7	δ_{27}	−1.59	−1.92
	6	δ_{26}	−4.55	−5.03
	5	δ_{25}	+1.25	+0.95

[a] Parametric values in column I were obtained by subtracting the various shifts in naphthalene from values at corresponding positions in quinoline and isoquinoline, while column II is the results of a linear regressional treatment of the benzenoid shifts in all of the azanaphthalenes. The linear regressional results are obtained from the population matrix given in Table IV.

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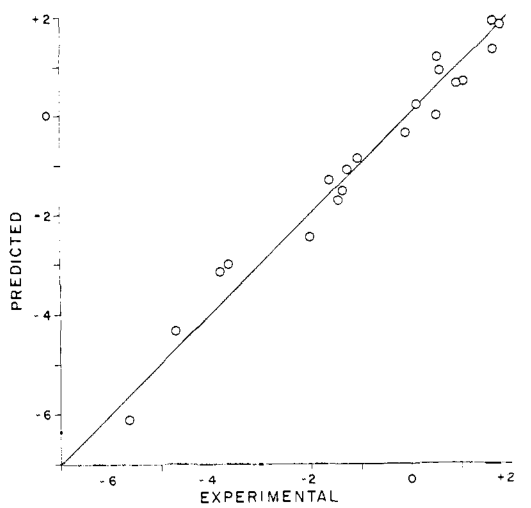

Figure 1. This plot of predicted *vs.* experimental chemical shifts for benzenoid carbons in a collection of monoaza- and diazanaphthalenes indicates the success of using the additive parameters contained in Table II for predicting long range effects upon carbon-13 chemical shifts.

results are contained in Table III. The reasonable agreement between the predicted and experimental values given in Table III therefore constitutes the basis upon which the uncertainties in the remaining assignments were eliminated.

Table III. Predicted Shifts for Otherwise Unassignable Carbons in the Diazanaphthalenes

Compound and item no.	Position	$\delta_{C^{13}}$ in ppm	Predicted $\delta_{C^{13}}$ I	Predicted $\delta_{C^{13}}$ II
Phthalazine				
27	5,8	+1.84	+1.89	+1.84
28	6,7	−4.68	−3.58	−4.39
Cinnoline				
32	5	+0.59	+1.41	+1.17
34	7	−3.62	−2.83	−3.00
Quinazoline				
40	5	+1.10	+0.36	+0.67
42	7	−5.63	−5.79	−6.11

Having completed all the assignments, the best possible set of nitrogen positional parameters was obtained with a standard linear regressional analysis. This was undertaken to determine the statistical significance of the various parameters and their reliability in treating all of the azanaphthalenes studied. The linear expression used in this analysis is characterized by eq 1,

$$\delta(j) - \delta_0(j) = \sum_i p_{ij}\delta_{ij} \tag{1}$$

where $\delta_0(j)$ is the reference naphthalene shifts at the α $[\delta_0(j = 5 \text{ or } 8) = +0.44$ ppm] and β $[(\delta_0(j = 6 \text{ or } 7) = +2.56$ ppm)] carbons. The experimental values $\delta(j)$ must be corrected with $\delta_0(j)$ to eliminate the effect of the bridgehead carbons at the α and β position (*i.e.*, j = 5 or 8 for α and j = 6 or 7 for β carbons). Implicit in this correction is the assumption that the effect of ring fusion on the peripheral benzenoid carbons is the same in every compound. Populational coefficients either 0 or 1 are given by the population matrix, p_{ij}, and δ_{ij} is the substituent shift parameter. The index "i" indicates whether the nitrogen atom is at the 1 position (quinoline type) or 2 position (isoquinoline type), while the position of the observed carbon is designated with j. The populational matrix is given in Table IV. The results of the regressional analysis are contained in Table II under parameter set II. The standard deviation in the over-all fit is 0.49 ppm and the multiple correlation coefficient is R^2 = 0.989 indicating a successful fit of data which are plotted as predicted *vs.* experimental in Figure 1.

Table IV. Population Matrix Used for Linear Regression Analysis

	Position	P_{15}	P_{16}	P_{17}	P_{18}	P_{25}	P_{26}	P_{27}	P_{28}
Quinoline	5	1	0	0	0	0	0	0	0
	6	0	1	0	0	0	0	0	0
	7	0	0	1	0	0	0	0	0
	8	0	0	0	1	0	0	0	0
Isoquinoline	5	0	0	0	0	1	0	0	0
	6	0	0	0	0	0	1	0	0
	7	0	0	0	0	0	0	1	0
	8	0	0	0	0	0	0	0	1
Phthalazine	5,8	0	0	0	0	1	0	0	1
	6,7	0	0	0	0	0	1	1	0
Quinoxaline	5,8	1	0	0	1	0	0	0	0
	6,7	0	1	1	0	0	0	0	0
Quinazoline	5	1	0	0	0	0	0	0	1
	6	0	1	0	0	0	0	1	0
	7	0	0	1	0	0	1	0	0
	8	0	0	0	1	1	0	0	0
Cinnoline	5	1	0	0	0	1	0	0	0
	6	0	1	0	0	0	1	0	0
	7	0	0	1	0	0	0	1	0
	8	0	0	0	1	0	0	0	1

As the positional parameters exhibit spatial relationship between atoms separated by as many as five bonds (*e.g.* consider δ_{26}), the high degree of reproducibility is considered to be particularly significant. It is interesting that a nitrogen atom in a given structural arrangement should have such a constant effect upon the electronic environment of a carbon atom so far removed from the nitrogen atom. Furthermore, these reproducible structural features in the carbon-13 shift data are of considerable importance in establishing routine analytical procedures for identification of heterocyclic compounds.

C. **Anthracene, Acridine, and Phenazine.** The carbon-13 resonance peaks for the tricyclic compounds were assigned on the same basis as in the bicyclic molecules and their chemical shifts also appear in Table I. Bridgeheads were assigned on the basis of smaller proton splittings and in acridine the negative α nitrogen parameter distinguishes C-11,14 from C-12,13. Items 48 and 54 can further be characterized from unique relative peak intensities. The remaining assignments depend upon the selective proton decoupling technique.

The chemical shifts in anthracene at the bridgehead, α and β positions (−3.74, −1.60, and +2.98 ppm, respectively) exhibit a trend which is similar to the corresponding values (−5.20, +0.44, and +2.56 ppm) in naphthalene, and it is felt that this further corroborates the above assignments of these three peaks. Using the anthracene shifts and the long range positional parameters given in column II in Table II, we predict that the order of outer ring shifts in acridine should be C-1,8 = −3.33 ppm (−1.03); C-4,5 = −1.82 ppm (−1.81); C-2,7 = −0.66 ppm (+0.17); and C-3,6 = +2.33 ppm (+3.03). The experimental values are given in parentheses to facilitate a comparison with the predicted shifts. In phenazine the predicted and experimental values (in parentheses) are $\alpha = -3.55$ ppm (−2.42) and $\beta = -1.31$ ppm (−1.78). The greatest discrepancy in acridine comes at the C-1,8 position where the predicted shift is downfield from the experimental one. A similar effect is noted in the α position of phenazine. These deviations indicate that the additional ring in the aza-anthracenes is apparently moderating the perturbing effect of nitrogen atoms upon the nearest benzenoid carbon. While the diazanaphthalene parameters are inadequate to account for the C-1,8 shift in acridine and the α-shift in phenazine, there is reasonable correlation between the predicted and observed values for all the remaining positions. This agreement confirms the assignments made on the basis of proton-decoupling information.

Discussion of Results

The two wave functions used previously[10] to study carbon-13 chemical shifts in heterocycles were the SCF–MO–CNDO/2 wave functions of Pople[7–9] and the EHT of Hoffman.[3] The former function utilizes self-consistence field methods, and therefore probably gives a more reliable prediction of charge density features. On the other hand the CNDO/2 method ignores overlap in the normalization process and this can result in artificially large variations in the bond-order terms about the bridgehead position. Alger, Grant, and Paul[2] discussed the effect which these approximations can have upon the predicted carbon-13 shifts at the bridgehead and exhibited the need for properly normalized wave functions if one is to compare calculated carbon-13 shifts of bridgeheads with those of peripheral carbons. The CNDO/2 results of Bloor and Breen[5] exhibited this problem which one can have with bridgehead carbons and led them to conclude that the simple correlation with charge densities was superior to the complete chemical shift calculation using the formulation of Karplus and Pople.[6] By employing overlap in the normalization procedure the EHT wave functions avoid the normalization problem for bridgehead carbons, and one may arbitrarily vary the ionization potentials in an empirical way to introduce some of the SCF features handled directly in the SCF–MO–CNDO approach. Equation 2, taken from Cusachs and Reynolds[30] gives the relationship between the ionization potentials (IP) used as input in the EHT program and *B*, initially the formal charge on the atom. In this work *B* is taken to be an arbitrary parameter for varying the effective electronegativity of 2s and 2p carbon orbitals.

$$\begin{aligned} \mathrm{IP\,(2s)} &= -21.16 - 11.56B \\ \mathrm{IP\,(2p)} &= -11.20 - 11.56B \end{aligned} \qquad (2)$$

Table V. Naphthalene Carbon-13 Chemical Shifts Using Various MO Wave Functions

	Position	$\sigma_p^{(1)}$	$\sigma_p^{(2)}$	Total[a]	Experimental[a]
CNDO/2	9	−4.27	−25.09	−29.36	−5.20
	α	+1.06	+1.45	+2.51	+0.44
	β	+0.28	+0.55	+0.83	+2.56
Simple EHT	9	−5.90	−17.13	−23.03	−5.20
$B = 0$	α	+2.66	+4.38	+7.04	+0.44
	β	+1.98	+4.79	+6.77	+2.56
EHT	9	+5.71	−12.20	−6.49	−5.20
	α	−2.66	+2.61	−0.05	+0.44
$B = +0.075$	β	+0.88	+4.69	+5.57	+2.56

[a] Taken with respect to benzene.

Table V summarizes the predicted chemical shifts in naphthalene relative to benzene for the CNDO/2 and two EHT treatments.[31] Note that both the CNDO/2 and simple EHT calculations predict the bridgeheads to occur at −29.36 and −23.13 ppm, respectively, while the experimental value is −5.20 ppm. Furthermore, both methods CNDO/2 ($\alpha = +2.51$, $\beta = +0.83$ ppm) and simple EHT ($\alpha = +7.05$, $\beta = +6.78$ ppm) predict the α carbon to be upfield from the β carbon contrary to experimental results. From Table V it is seen that these discrepancies are the result of both the one-center, $\sigma_p^{(1)}$, and two-center $\sigma_p^{(2)}$, terms.[32] The extent of these discrepancies in the CNDO/2 approach has already been given[5] for most of the compounds under study, and we present the results of the simple EHT ($B = 0$) theoretical treatment of the data in Figure 2. As with the results of Bloor and Breen[5] the greater deviations from the perfect agreement line are noted for bridgehead carbons. To account for some of the discrepancies in these two treatments, we again return to a detailed consideration of the naphthalene molecule and draw attention to the MO parameters obtained for this molecule and given in Figure 3. Consider the depletion of charge at the bridgehead in both the CNDO/2 and simple EHT treatments as this accounts for the negative $\sigma_p^{(1)}$ values in Table V. One should also note in the CNDO/2 calculation the large π bond orders about bridgehead carbons. These parameters lead to very negative $\sigma_p^{(2)}$ values (see Table V). The parameters obtained from the modified EHT calculation are also presented in Figure 3 and attention is drawn to the variations in both charge and bond orders resulting from using a value of $B = 0.075$ for orbitals at bridgehead carbons. Increased electronic charge at the bridgehead (it is acknowledged that the parameters are probably overcorrected) and relatively small changes in the bond orders combine to give $\sigma_p^{(1)}$ and $\sigma_p^{(2)}$ terms in Table V which predict the correct magnitude for the bridgehead shift and the correct ordering of the α and β shifts. Using this $B = 0.075$ parameter, the chemical shifts of all compounds were recalculated and the results are portrayed in Figure 4. The results for the carbocycles (naphthalene and anthracene) now correlate quite well, as the value of *B* was selected arbitrarily in these nonnitrogen systems to give the best agreement. This empirical approach also leads to improvement in the

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(30) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, 43 S 160 (1965).

(31) The authors wish to express appreciation to R. Hoffmann and G. A. Segal for providing computer programs No. 30 (EHT) and 91 (CNDO-SCF), respectively, through the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

(32) This division of the paramagnetic term into two parts follows the convention used in ref 2. The one-center contribution, $\Delta\sigma_p^1$, arises primarily from changes in the charge densities while the two-center term, $\Delta\sigma_p^2$, is dominated by bond-order variations. Increased electronic charge makes $\Delta\sigma_p^1$ more positive while increased bond orders cause σ_p^2 to shift to lower fields. See ref 10 for a more detailed discussion of the contribution of the various factors in the shielding expression.

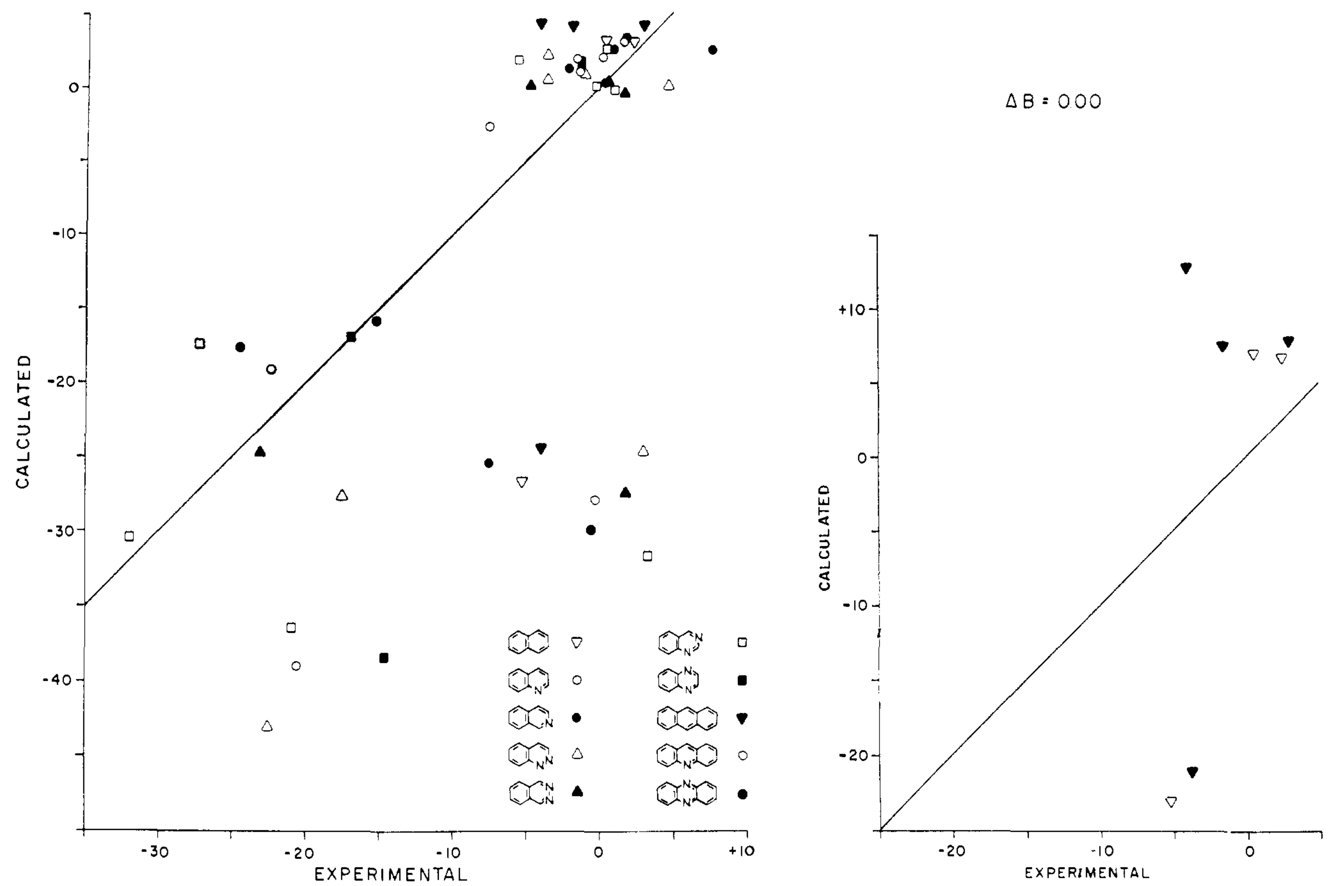

Figure 2. Carbon-13 chemical shifts calculated by the simple EHT method with $B = 0$ are plotted *vs.* the experimental values for the compounds indicated.

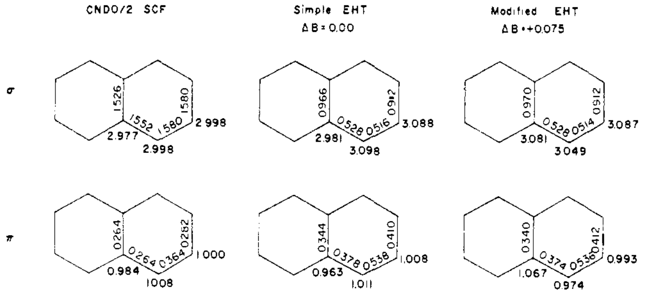

Figure 3. Molecular orbital parameters obtained for naphthalene by the CNDO/2 and two EHT calculations include charge densities (outside of rings) and bond orders (inside of rings).

heterocyclic shifts, especially at bridgehead carbons. While it is hazardous to extract too much meaning from an approximate empirical method of this type, which may be overcorrected in both charge and bond orders, the calculation of carbon-13 shifts nevertheless does suggest the type of alterations which appear to be needed in the approximate wave functions to give the proper agreement with experimental shifts. Furthermore, as these changes are of a nature which reflect expected weaknesses in the approximate wave functions, it is felt that the experimental carbon-13 shift data make an important contribution in specifying some of the limitations of approximate quantum mechanical treatments of relatively large molecules.

The highly reproducible long range nitrogen positional parameters observed in the benzenoid ring system does pose some interesting possibilities and suggests an approach for modifying the CNDO/2 treatment of the data. First, aromatic systems are well known for their sensitivity to long range inductive and resonance effects, and here we have evidence that these effects are very reproducible in related molecules. Using the CNDO/2 program, such effects were explored theoretically by comparing the various calculated shifts each referred to the calculated shift in the parent molecule, either naphthalene or anthracene. By adjusting the CNDO/2 results in the same manner as the substituent parameters were defined, one can capitalize on the desirable features of this approach while avoiding through mutual cancellation the large discrepancies arising from neglect of overlap in the bridgehead shifts of both carbocyclic and heterocyclic systems. The result of this treatment of the data can be visualized in Figure 5. A reasonable correlation between predicted and experimental values is found with a reduction in the scatter from that noted even in the relatively successful modified EHT ($\beta = 0.075$) calculation given in Figure 4. The slope of the correlation line unfortunately deviates significantly from a perfect agreement line, and it is not known whether this reflects the limitations in the average energy approximation or results from errors inherent in the referencing of the nitrogen compounds to their carbocyclic parents. Nevertheless, this calculation does suggest that the changes in carbon-13 chemical shifts are due to resonance and inductive effects which would be approximated with some degree of validity by the CNDO/2 treatment. The charge densities and bond orders ob-

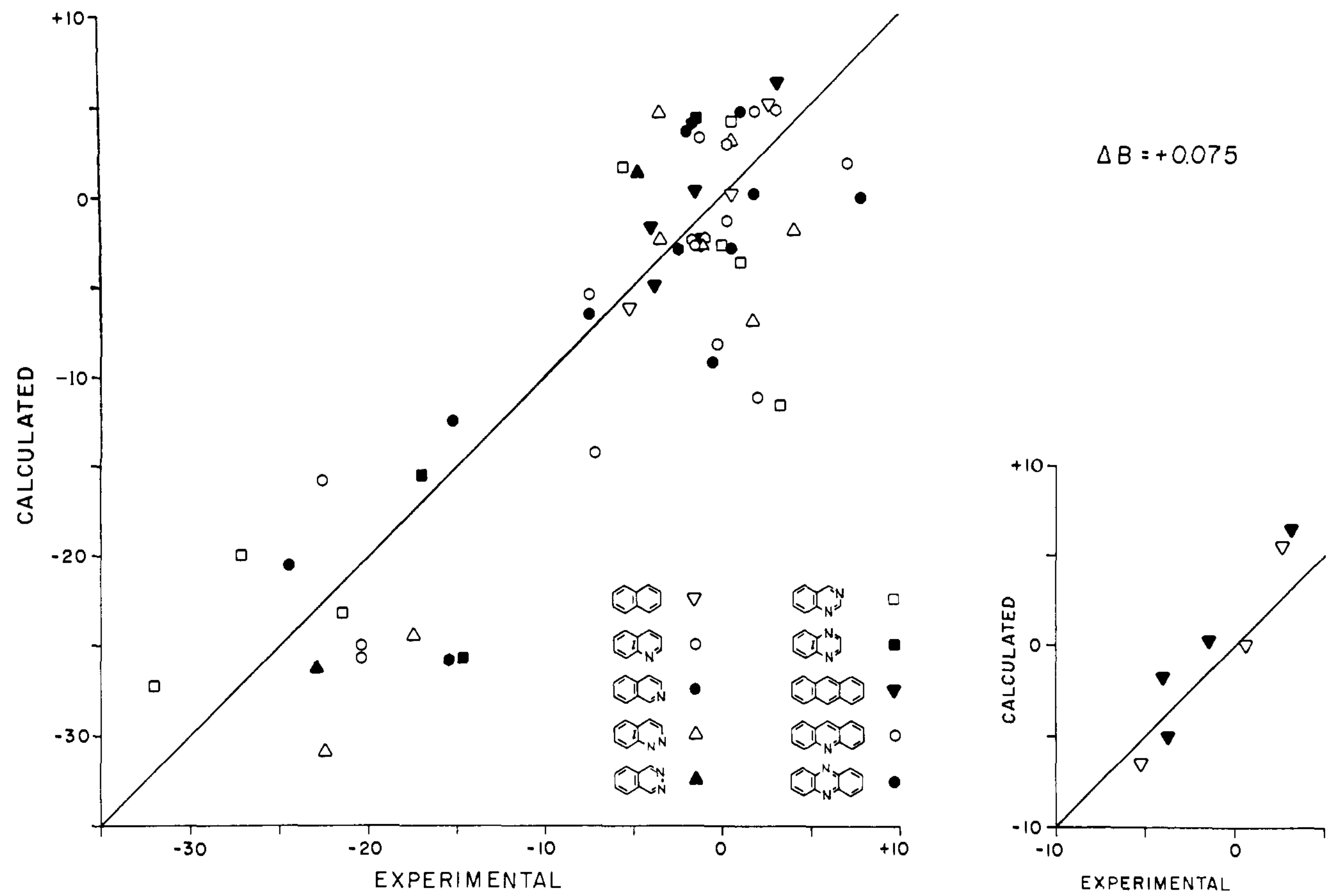

Figure 4. Carbon-13 chemical shifts calculated by a modified EHT method with $B = 0.075$ are plotted *vs.* the experimental values for the compounds indicated.

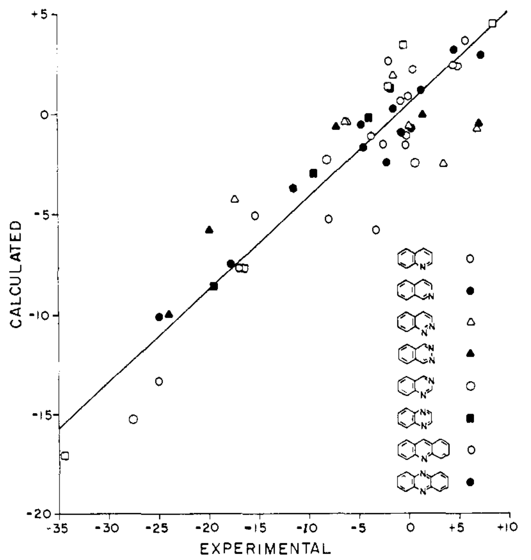

Figure 5. CNDO-predicted chemical shifts are plotted *vs.* experimental values for the compounds indicated. Both predicted and experimental quantities were first referenced to the corresponding predicted and experimental values found in the carbocyclic parent which is naphthalene for the bicycles and anthracene for the tricycles.

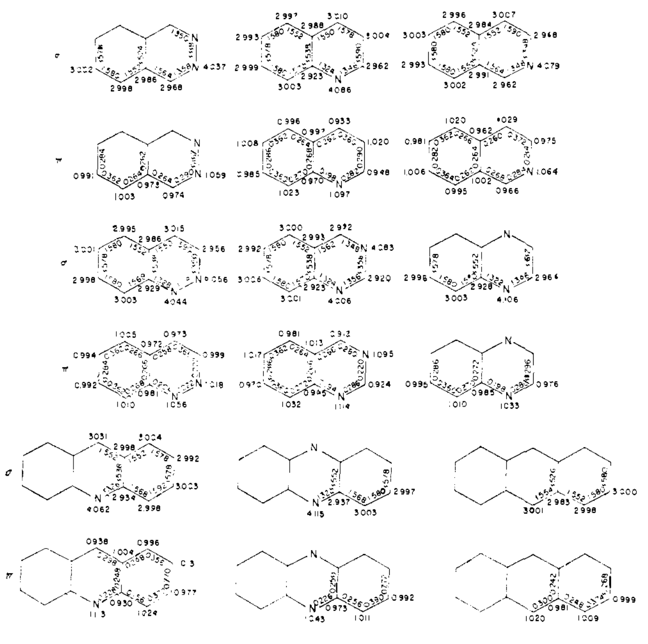

Figure 6. Molecular orbital parameters obtained from the CNDO/2 program inclde both σ and π charge densities (outside of ring) and bond orders (inside of rings). The slight difference in charge densities reported in this figure and in ref 5 are not significant and probably arise from small differences in molecular geometries. Idealized geometries were used in all calculations reported in this work.

tained with this treatment are summarized in Figure 6 and form the basis of the results given in Figure 5.

The significance of the theoretical calculation lies not in the fact that a perfect correlation is or is not achieved, but that carbon-13 chemical shifts reflecting many of the important electronic features are anticipated at least crudely by approximate molecular orbital calculations.

The results of this study also suggest that long range inductive and resonance effects may in many instances be expected to be additive in their influence on various chemical and physical properties.

Related Theoretical Treatments[33]

The recent paper of Adam, Grimison, and Rodriquez[34] raises several questions regarding the theoretical basis of the calculations in this work, and therefore comments are appropriate. These workers surveyed various approaches and approximations which have been used to date in theoretically treating carbon-13 chemical shifts and came to the following conclusions. (1) An improved correlation of experimental shifts is realized if extended Hückel wave functions are first multiplied by the square root of the overlap matrix. This calculational detail is justified in part as it compensates for orthogonalization problems introduced into the basic chemical shift derivation. Conceptionally, at least, this feature is related to the corrections incorporated in eq 11 of ref 10a. Such orthogonalization corrections are required to make the EHT wave functions which include overlap compatible with the chemical shift expressions which have been derived neglecting overlap. (2) Adam, *et al.*,[34] further stress the importance of possible variations in ΔE, the average excitation energy, in accounting for differences between five- and six-membered nitrogen heterocycles. Our previous work[35] also confirmed the reasonableness of this suggestion, and it is now evident that changes in ΔE are important when comparing the shifts of charged and neutral species or of five and six-membered ring systems. (3) The diamagnetic term was claimed to be of considerable significance in accounting for carbon-13 chemical shifts in the nitrogen heterocycles. Predicted shifts ranged from -10.33 for C-2 in pyrimidine to $+1.52$ for C-3,4 in the pyrrole anion. These shifts along with the other compounds considered,[34] follow closely the charge densities of the carbon atoms under study. In the case of the two extremes just cited, the calculated total charges are 3.26 and 4.14 electrons, respectively, giving a 13 ppm/electron dependence for the diamagnetic term. This theoretical estimate compares reasonably well with the theoretical result of 17.8 ppm/electron obtained by Cheney and Grant[36] for the diamagnetic term. We, therefore, raise no question with the chemical-shift calculation of the diamagnetic term and acknowledge that shifts of this magnitude could result from the calculated charges. The only issue which needs to be resolved is whether or not the EHT method is reliably predicting the correct charge density. As other SCF–MO calculations[37] predict much smaller charge polarization effects in these same molecules, it is reasoned that the EHT charge values are too large by a factor of three or fourfold, and the diamagnetic contribution to the chemical shift can be expected to decrease concomitantly to about 2–3 ppm. This would only constitute about a 5% correction on the 50–60 ppm range noted in the five- and six-membered heterocycles considered. As a standard deviation of 6.4 ppm was reported[34] for the best fit, a 2–3 ppm diamagnetic correction would not represent a contribution of any consequence. (4) It was also suggested in ref 34 that all two-center integrals should be neglected in the chemical shift formulation as they introduce serious gage problems[38] into the calculation. These authors claim that the Karplus and Pople[6] formulation given as eq 8 in ref 34 follows directly from their eq 7 which does not include any two-center integrals. A closer assessment of the situation, however, reveals that the same two-center integrals of the type given by eq 7 in ref 10a and by eq 11 given by Bloor and Breen[5] must be considered in order to obtain the free valence term which appears in the Karplus–Pople[6] π electron formulation. Alger, *et al.*,[2] has specified the types of two-center integrals which can be evaluated (eq 10 in ref 2) and still avoid the gage problem. These approximations are identical with those of Karplus and Pople[6] and Bloor and Breen,[5] and, therefore, the calculations used in this paper reside on the same theoretical basis. The treatment of nitrogen heterocycles requires the extension of the features of the Karplus–Pople[6] formulation to include the σ electrons, as well as π electron systems. This is the only significant difference between the two approaches. It probably should be noted that the orthogonalization approximation of Adam, *et al.*,[34] can be expected to produce the same errors in the predicted bridgehead shifts as found for CNDO/2 wave functions in the previous section whenever two-center terms are considered. Equation 11 of ref 10a, on the other hand, avoids inordinately large π-bond orders about bridgehead carbons and the sizeable negative error in predicted shifts.

In summary it appears that the several theoretical treatments of five- and six-membered nitrogen heterocycles are all based on the works of Karplus and Pople and therefore, in many respects, are really quite similar. This similarity results primarily from the fact that all workers have stressed the dominant charge polarization features of the calculation. The differences on the other hand may be summarized as follows: Adam, *et al.*,[34] have neglected certain two-center terms included in ref 5, 6, and 10, but have emphasized the importance of the diamagnetic term, and qualitatively stressed the importance of variations in ΔE. Pugmire and Grant on the other hand have explored extensively the importance of changes in bond orders upon the chemical shift, especially at α carbons to protonated nitrogen atoms.

It now appears from the work of Jones, *et al.*,[39] that both variations in bond order and ΔE are needed to account for anomalous upfield protonation shifts at carbons adjacent to nitrogen atoms. Taken separately bond-order variations and the effect of changes in excitation energy on only one-center chemical shift terms,

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(33) This section was added in response to a referees request that clarification be given on the similarities and differences existing between the theoretical approach used in ref 34 and the theory used in this work based on ref 2 and 10.

(34) W. Adam, A. Grimison, and G. Rodriquez, *J. Chem. Phys.*, **50**, 645 (1969).

(35) Adam and coworkers were acknowledged in ref 10b for their suggestion that this approach would improve the theoretical fit of the experimental data.

(36) B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 5319 (1967).

(37) See, for example, ref 5 and M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).

(38) A number of workers (see particularly J. A. Pople, *Proc. Roy. Soc., Ser. A*, **239**, 541 (1957); *J. Chem. Phys.*, **37**, 53, 60 (1962)) have pointed out that gage invariant orbitals must be used in chemical shift calculations or else one must restrict consideration only to ring currents centered on the atom of interest. This restriction, however, does not limit consideration of some two-centered integrals, as discussed in detail by Alger, Grant, and Paul.[2]

(39) A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).

both fail to account for the large observed α-protonation shifts. On the other hand bond-order terms, arising from important two-center integrals, are required to transfer to the α carbon the effect of the changes in the effective ΔE arising primarily in protonation from a change in the n–π^* or NH–π^* energy separation. It is now felt that a combination of both features is required to explain best anomalous shifts in α carbons at the present time.

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An Electron Spin Resonance Study of the Kinetics of Recombination of Tri-*t*-butylcycloheptatrienyl Radicals[1]

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Abstract: Few measurements of recombination rate constants for hydrocarbon free radicals in liquid solution have been reported. The goal of this work is to measure the rate of recombination of the tri-*t*-butylcycloheptatrienyl radical using a simple esr technique. This free radical is generated by photochemical cleavage of hexa-*t*-butylbicycloheptatrienyl in *n*-pentane. The recombination rate has been measured ($-112° \leqslant t \leqslant +22°$) by terminating the illumination and monitoring the second-order decay of the esr signal on a strip-chart recorder. Absolute rate constants are obtained by comparison of the steady-state esr intensity with that of a solution of di-*t*-butylnitroxide of known concentration. Typical approximate rate constants are $3 \times 10^4 M^{-1}$ sec^{-1} at −105° and $3 \times 10^5 M^{-1}$ sec^{-1} at +22° and the Arrhenius activation energy is 1.7 ± 0.3 kcal/mol. The rate of recombination is compared with that of other hydrocarbon free radicals in solution.

Although the rates of free-radical reactions in liquid solution are of great interest,[3] few measurements of recombination rates have been reported for small, *i.e.*, monomeric, hydrocarbon radicals.[4] Of these only the study of ethyl radical has employed esr spectroscopy.[5]

We have therefore investigated the recombination kinetics of tri-*t*-butylcycloheptatrienyl radical. The esr spectrum of this radical has been discussed elsewhere.[6] This choice of a system (1) leads to the utilization of a much simpler esr technique than that required for the alkyl radicals[4,5] since the recombination rate constant is considerably smaller and (2) reflects our continuing interest in the esr of π-electron free radicals containing seven-membered rings.[6,7]

Experimental Section

Most of the experimental details have been described elsewhere.[6] These include the synthesis of hexa-*t*-butylbicycloheptatrienyl, sample-preparation technique, materials used as solvents, esr spectrometer employed, and the apparatus to vary the sample temperature.

Rate constants for radical recombination were measured as follows. Deoxygenated samples of hexa-*t*-butylbicycloheptatrienyl in *n*-pentane were placed in a Varian Associates dual cavity and were illuminated *in situ* using the full output of a Hanovia 140W high-pressure mercury lamp (Model SH). The esr spectrum of the tri-*t*-butylcycloheptatrienyl radical was detected. Sample illumination was terminated by means of a shutter. The decay of the peak height of the central component of the esr spectrum was monitored using a Honeywell Electronik 19 strip-chart recorder.[8] Recombination rate constants, k_{-1}, were obtained from the slopes of the plots of C_0/C *vs.* time, which were linear.

Values of the initial (steady-state) radical concentrations, C_0, were determined by comparison of the integrated intensity of the esr spectrum of the recombining radical with that of a known concentration of the stable di-*t*-butyl nitroxide radical. (The concentration of this standard was measured spectrophotometrically).[9] The standard sample was placed in the 400 Hz channel of the dual cavity and its spectrum was recorded simultaneously with that of tri-*t*-butylcycloheptatrienyl. Intensities were compared in terms of the product of the peak heights and the square of the line widths of the central components of the first-derivative spectra. An approximate study of the line shapes for the nitroxide and tri-*t*-butylcycloheptatrienyl radicals revealed that these are the same within experimental scatter[9b] and so a line shape factor does not enter into the intensity measurement.

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(1) Supported by the U. S. Army Research Office, Durham.

(2) Alfred P. Sloan Research Fellow.

(3) C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(4) (a) G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957); (b) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960); (c) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964); (d) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(5) Two closely related esr investigations are (1) a study of cyanoalkyl radical recombination (S. Weiner and G. S. Hammond, *ibid.*, **90**, 1659 (1968)) and (2) a study involving a pseudo second-order decay of CH_3-(aq) (D. Mickewich and J. Turkevich, *J. Phys. Chem.*, **72**, 2703 (1968)).

(6) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968).

(7) (a) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *J. Amer. Chem. Soc.*, **87**, 3527 (1965); (b) W. V. Volland and G. Vincow, *J. Chem. Phys.*, **48**, 5589 (1968); (c) W. V. Volland and G. Vincow, *J. Amer. Chem. Soc.*, **90**, 4537 (1968); (d) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *ibid.*, in press; (e) M. D. Sevilla, S. H. Flajser, G. Vincow, and H. J. Dauben, Jr., *ibid.*, in press.

(8) The full-scale pen-response time for this recorder is 0.3 sec. The response time of the esr spectrometer was never larger than one-tenth of the first half-life of the decaying signal.

(9) (a) A. K. Hoffman and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961); (b) for further details see M. L. Morrell, Ph.D. Thesis, University of Washington, Seattle, Wash., 1967.