Anal. Calcd for $C_{20}H_{16}N_2O_7S$: C, 56.09; H, 3.77; N, 6.54. Found: C, 55.98; H, 3.69; N, 6.32.

2-Nitro-9-fluorenyl *p*-Toluenesulfonate (VII). To a stirred solution of 17.3 g of 9-diazo-2-nitrofluorene[7] in 320 ml of acetonitrile was added 12.4 g of dried *p*-toluenesulfonic acid at room temperature. The mixture was stirred for an additional 30 min, after which time the product was isolated by filtration and washed with ether. The crude yield was 16.2 g (58.2%). After crystallization from acetone the product melted at 132.5–133.5 dec. The infrared spectrum showed absorption at 6.52 (s) and 7.54 μ (s), characteristic of aromatic nitro, and at 7.40 (s), 8.43 (m), and 8.52 μ (s), characteristic of the sulfonate ester group.[4]

Anal. Calcd for $C_{20}H_{15}NO_5S$: C, 62.98; H, 3.96. Found: C, 62.86; H, 3.78.

2-Nitro-9-fluorenyl Acetate. A solution of 3 g of VII in 100 ml of glacial acetic acid was gently refluxed for 1 hr. The solution was cooled and diluted with 100 ml of water, and the product was filtered and purified by crystallization from methanol; yield, 2.02 g (95.4%), mp 148–149.5°. The infrared spectrum showed absorption at 6.57 (s) and 7.48 μ (s), characteristic of aromatic nitro, and at 5.72 (s), 8.20 (s), and 9.65 μ (s), characteristic of the acetate group.

Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.65; H, 4.10; N, 5.30.

This compound was also prepared by stirring 3 g of 9-diazo-2-nitrofluorene in 80 ml of glacial acetic acid at room temperature for 30 min. The product was isolated by dilution with 80 ml of water followed by filtration. After crystallization from methanol the yield was 2.9 g (85.1%).

Kinetic Measurements. The kinetic procedures have been described previously[2] as has the calculation of activation parameters.

Analysis of Kinetic Data to Obtain K and k_c. The kinetic data were analyzed according to eq 1 using the weighted least-squares procedure previously described.[2,17] Uncertainties in k_c and K listed in Table II are standard deviations calculated by the simple least-squares procedure. Uncertainties in activation parameters and thermodynamic quantities were calculated using standard procedures.[17]

Acknowledgment. We are grateful to the National Science Foundation (Grants G-19842 and GP-3355) for support of this work.

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(17) L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961.

Structure of Some Carbanions as Deduced from Nuclear Magnetic Resonance Study of Their Protonation Products

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Abstract: The nmr spectra of 9,10-dihydroanthracene and its 9-ethyl derivative have been investigated. It has been shown that the former molecule undergoes a rapid oscillating motion through the planar configuration at temperatures as low as −55°. Introduction of the alkyl group either quenches this movement, or greatly favors one stereoisomer, even at 40°. These results and also those obtained from a study of the nmr spectrum of the 9-ethyl derivative monodeuterated in the 10 position have permitted a discussion of the structure of the carbanions derived from 9,10-dihydroanthracene. Thus, it has been shown that the anion is not planar. Its 9-ethyl derivative possesses the alkyl group preferentially in equatorial position and the Li^+ ion in the respective ion pair is located on the same side as the ethyl group.

In connection with our studies of the reactivity and structure of carbanions we investigated the negative ions derived from 9,10-dihydroanthracene and its derivatives. This work led us to study the nmr spectra of 9,10-dihydroanthracene and its 9-ethyl derivative. The results revealed that either a rapid "flapping" motion of the former molecule is quenched by substitution of one of the 9-hydrogens by the alkyl group or one stereoisomer of the alkyl-substituted compound is particularly favored. Moreover, collating all the evidence, we arrived at interesting conclusions about the structure of the respective carbanions.

Experimental Section

9,10-Dihydroanthracene was acquired commercially. The compound contained a small amount of anthracene which was removed by refluxing the impure material with maleic anhydride in xylene solution. After washing with water to remove the adduct and excess of maleic anhydride, the dihydroanthracene was isolated and recrystallized from methanol. The ultraviolet spectrum of the purified compound showed the presence of less than 0.1% of anthracene.

Commercial anthracene (chemically pure) was twice crystallized from toluene and sublimed under high vacuum before being used.

Ethyllithium in benzene solution (Foote Mineral Co.) was purified under high vacuum by repeated crystallization, using the procedure described elsewhere.[1] The purified solution, never exposed to air, was placed in ampoules equipped with breakseals and the solvent was removed by evacuation before sealing off the container.

Addition of ethyllithium to anthracene was accomplished by adding an equimolar amount of the lithium compound to a solution of anthracene in thoroughly purified tetrahydrofuran. The reaction was carried out in an evacuated ampoule at room temperature. The resulting lithium salt was converted into the hydrocarbon by adding an excess of deaerated water or isotopically pure D_2O. The ampoule was then opened to air and the hydrocarbon recovered. The resulting material contained a small amount of unreacted anthracene, but otherwise it was found pure.

The nmr spectra were taken on a A-60-A Varian spectrometer using deuterated chloroform or deuterated THF as solvent. The former compound was virtually free of any hydrogen-containing impurities, but the spectrum of the deuterated THF showed two single lines at 104 and 215 cps (δ 1.73 and 3.58, respectively) which were attributed to the partially hydrogenated ether. These lines did not interfere with the investigated spectra. All the reported chemical shifts are related to tetramethylsilane used as an internal standard and, unless otherwise stated, the spectra were taken at 40°.

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(1) M. Van Beylen, D. N. Bhattacharyya, J. Smid, and M. Szwarc, in press.

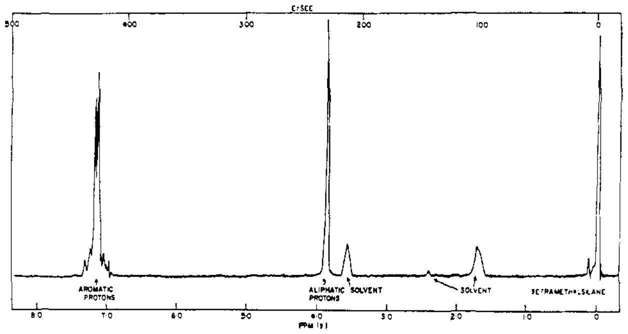

Figure 1. Spectra of 9,10-dihydroanthracene in tetrahydrofuran-d_8.

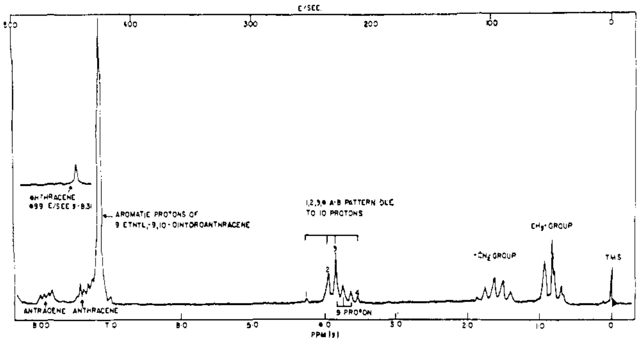

Figure 2. Spectrum of 9-ethyl-9,10-dihydroanthracene in CCl_3D.

Results and Discussion

The spectrum of 9,10-dihydroanthracene in CCl_3D revealed two extremely sharp lines at 234 and 432 cps (δ 3.90 and 7.20, respectively) as compared with δ 3.87 and 7.18 reported in the Varian handbook. The integration led to the ratio 1:2.0 for the aliphatic to aromatic protons. At lower temperatues the lines, although still not split, were broadened and were slightly shifted down field. For example, at $-55°$ (the lowest temperature investigated) the chemical shifts, δ, were 3.95 and 7.32, respectively. In deuterated THF solution the aromatic, but not the aliphatic, line was split, as shown in Figure 1, the separation being 2 cps. The relative heights of the two peaks remained independent of the direction of scanning, and their integration was as expected for eight aromatic protons. Apparently a weak H bonding with the ether affects differently the two types of protons. The sharpness of the line due to the 9,10-protons proves that the molecule rapidly vibrates through the planar configuration rendering the aliphatic protons equivalent even at $-55°$. An alternative explanation, *i.e.*, planarity of the molecule, is improbable.

The nmr spectrum of 9-ethyl-9,10-dihydroanthracene in CCl_3D is shown in Figure 2. The aromatic protons were again represented by a single sharp peak at 428 cps (δ 7.13). The spectrum of the ethyl group showed a triplet centered at 49 cps (δ 0.82) with $J = 7$ cps and a quintet at 97 cps (δ 1.62) again with $J = 7$ cps. The former is clearly identified as being due to the CH_3 group split by the CH_2 group. The latter is attributed to the CH_2 group split by the CH_3 group and by the 9-hydrogen, both couplings having the same J value. The integration of the triplet and quintet led to the ratio 2.94:2.00 as compared with the expected 3:2. The ratio of aromatic protons (corrected for the presence of anthracene) to those of ethyl group was found to be 8.3:5 (expected 8:5).

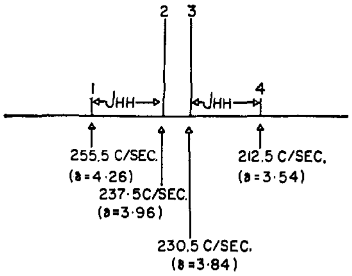

Figure 3. AB spectrum arising from the nonequivalence of the 10-protons of 9-ethyl-9,10-dihydroanthracene.

The spectrum of the 9-hydrogen was expected to be a triplet with J equal again to 7 cps. This was indeed found, the center being at 225 cps (δ 3.75), although the line expected at 232 cps merged with one peak of the pattern representing the 10-protons (see Figure 2).

The spectrum of the two 10-protons revealed an A–B pattern, shown schematically in Figure 3, proving that these protons are *not* equivalent any more. The center of this pattern, located at 234 cps (δ 3.90), coincided with the line of the aliphatic protons of 9,10-dihydroanthracene. This indicates that the nonequivalence of the two 10-protons in the ethyl derivative is either due to the inhibition of the "flapping" motion of the molecule, hindered by the presence of the alkyl group, or to a strong preference for one stereoisomer. We may assume, therefore, that one of the C-10 protons is axial most of the time, the other being equatorial. The coupling constant for these protons was found to be 18 cps, a value in agreement with that expected for geminal protons.

The chemical shift between the axial and equatorial protons may be calculated from the observed lines by using the equation[2]

$$(1\text{-}3)\ \text{shift} = \{(\delta_{\text{ax}} - \delta_{\text{eq}})^2 + J^2)\}^{1/2}$$

Since the (1-3) shift is found to be 25 cps and $J = 18$ cps, we find $\delta_{\text{ax}} - \delta_{\text{eq}} = 17.4$ cps. This value may be checked by calculating the ratio of the transition probabilities, *viz.*

$$\frac{\text{intensity of 1}}{\text{intensity of 2}} = \frac{1 - J\,\{(\delta_{\text{ax}} - \delta_{\text{eq}})^2 + J^2\}^{-1/2}}{1 + J\,\{(\delta_{\text{ax}} - \delta_{\text{eq}})^2 + J^2\}^{-1/2}}$$

The calculated ratio was found to be 1:6.1 compared with the experimental result of integration of 1:6.4.

Hence, the positions of the lines corresponding to the unperturbed 10-protons should be at 225.3 and 242.7 cps (δ 3.75 and 4.04, respectively). The former value coincides with that found for the chemical shift of the 9-proton, *viz.* 225 cps. This proves not only the correctness of our analysis but it indicates that of the two possible stereoisomers of 9-ethyl-9,10-dihydroanthracene one is greatly favored in the products of protonation of the respective carbanion.

It is reported in the literature[3] that the axial proton absorbs at a higher field than the equatorial, the difference, $\delta_{\text{eq}} - \delta_{\text{ax}}$, varying from 0.13 to 0.51 ppm, *i.e.*, from 8 to 30 cps. On this basis the observed line at 225 cps may be attributed to an axial 9-proton and,

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(2) See, *e.g.*, L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, p 89.

(3) See, *e.g.*, ref 2, p 116.

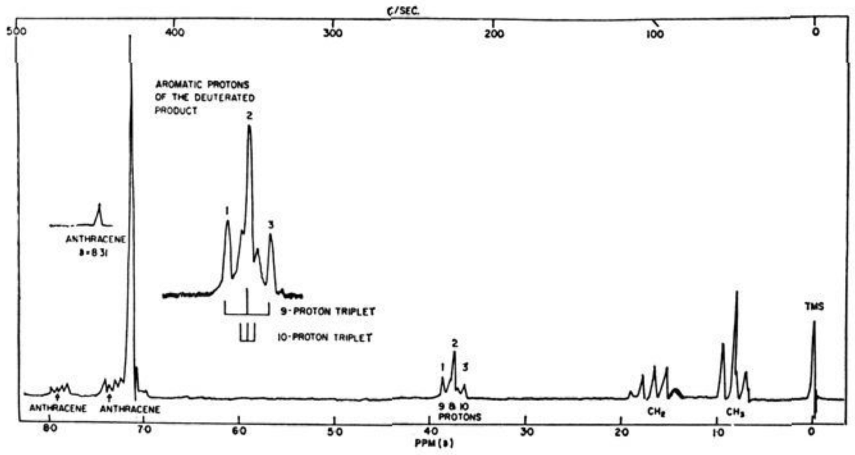

Figure 4. Spectrum of deuterated product in CCl_3D.

therefore, we may conclude that the ethyl group prefers an equatorial position. This seems to be reasonable—the equatorial stereoisomer is expected to be thermodynamically more stable. The above result does not permit us yet to make any definite conclusion about the stereochemistry of the respective carbanion. For example, our findings may be compatible with a planar structure of the anion.

To gain further insight into the structure of the carbanion, we investigated the nmr spectra of the products obtained by deuteration of the anion.

Examination of the ultraviolet spectra of the lithium salt of the ethyl-substituted carbanion in THF solution at 20° showed two peaks of approximately equal intensity, namely, λ_{max} 450 and 400 mμ. On cooling the solution to $-55°$ the 400-mμ peak disappeared while the intensity of that at λ_{max} 450 mμ increased. The above changes were found to be reversible. Discussion of the ultraviolet as well as the nmr spectra of the carbanions will be given in a forthcoming publication, but here we wish to emphasize that the same product was obtained whether the deuteration of the carbanion was accomplished at -70 or at $+55°$. The nmr spectra of both products were identical.

The spectrum of the deuterated product is given in Figure 4. The line corresponding to the aromatic protons again occurred at 428 cps (δ 7.13). It is important to notice that the spectrum corresponding to the ethyl group remained the same as that found in the protonated material. The CH_2 group was again represented by a *quintet* centered at 98 cps (δ 1.63) with $J = 7$ cps. This proves that the negative charge resides on the C-10 and that the change in the ultraviolet spectrum of the carbanion cannot be attributed to any tautomerism.

Further evidence for the above conclusion comes from the examination of the nmr spectra in the 9- and 10-proton region. The existence of a triplet (1,2,3) centered at 225 cps (δ 3.75) and the absence of the A–B pattern, proves that the D atom is located at the 10 position and not at the 9. The presence of the D atom at the 10 position should lead to another triplet with a lower coupling constant. The magnetic moment of the D nucleus is 0.15 of that characterizing a proton, and hence the coupling between an H and D atom should be reduced by the same factor when compared with that between two hydrogen atoms. The coupling constant between the nonequivalent 10-protons was found to be 18 cps and hence the expected coupling for the H–D is 2.7 cps. Inspection of Figure 4 shows the existence of two lines at 227 and 222 cps suggesting that they belong to a triplet centered at 224.5 cps (δ 3.75) with $J = 2.5$ cps. This, therefore, confirms the presence of a CHD group and indicates that the H atom is in an axial position.

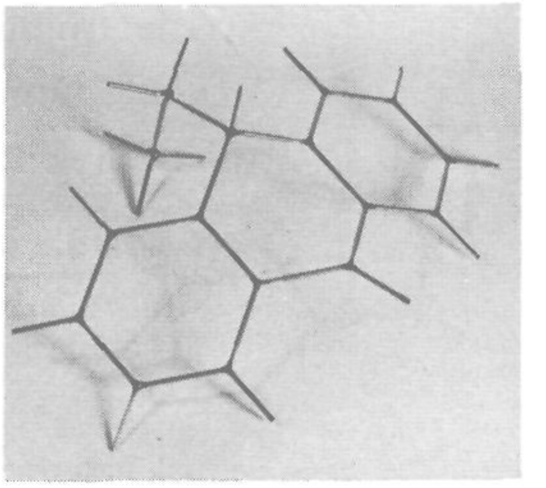

Figure 5. Model of the carbanion derived from 9-ethyldihydroanthracene indicating the equatorial position of the ethyl group and the sp^2 configuration of the carbanion.

The integration confirms the proposed assignment. The spectrum of the product deuterated at $-70°$ led to the ratio aromatic:(9,10):CH_2:CH_3 = 7.9:1.9:2.1:3.0. A similar ratio was obtained for the preparation at 55°.

The Structure of the Carbanions

The well-defined position of the 10-proton in the deuterated product derived from the 9-ethyl derivative of the carbanion proves that the latter species is not planar. Deuteration of a planar anion should lead to a mixture containing equal amounts of hydrocarbons having the 10-proton in either axial or an equatorial position. The molecule of the carbanion must, therefore, be bent, the ethyl group prefering the thermodynamically stable equatorial conformation. The lithium ion in an ion pair is probably located under the "roof" (see Figure 5) where it is stabilized by interaction with the π electrons of the aromatic rings. Deuteration (or protonation) takes place on the side of the Li^+ giving LiOD or LiOH and placing the original C–H in an axial position. This accounts for our observations.

Our present results do not permit us to decide whether the C-10 atom of the ethyl-substituted ion has sp^2 or sp^3 hybridization. However, the results to be reported later indicate that the former structure is more probable. It seems that the carbanion derived from the nonethyl substituted dihydroanthracene vibrates rapidly though its planar configuration and that the electronic structure of the C-10 atom in the dihydroanthracene ion approaches more the sp^3 hybridization than that in the ion of the ethyl derivative.[4]

Acknowledgment. This study was supported by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society.

[4] NOTE ADDED IN PROOF. It has been shown lately that change in the concentration of the hydrocarbon shifts uniformly the whole nmr spectrum relative to the TMS line without affecting the distance between individual peaks. Technical reasons forced us to investigate the spectrum of the ethyl-substituted dihydroanthracene at 20% w/v concentration instead of the 10% w/v used for the unsubstituted compound. This caused an upfield shift in the position of all protons; *e.g.*, the aromatic ones are then found at 428 cps as compared with 432 cps. Consequently, the "corrected" position of the AB center in the ethyl derivative does not coincide with the line for the aliphatic protons of the unsubstituted compound, the deviation being about 4 cps. This phenomenon does not, however, affect any of the conclusions reported in our paper.