

tween solute and solvent, and  $k$  is the Boltzmann constant. If  $E$  is small and remains constant, as in a homologous series of solvents, a plot of  $\ln B$  against the solvent surface tension should produce a straight line. From the slope of this line one can then calculate the radius of the cavity, which is essentially the radius of the solute molecule. Equation 1 has been found applicable to a number of systems,<sup>1-3</sup> as well as those where water is the solute in a series of normal alkane solvents from  $C_7$  to  $C_{16}$ .<sup>4</sup> From the latter systems, the molecular diameter of water was determined at 25 and 40°. Since the solubility of water in these hydrocarbons is very low ( $10^{-4}$  mole fraction), ideal solutions can be assumed.

From the Eyring absolute reaction rate theory, a quasithermodynamic expression for the diffusion coefficient  $D$  is

$$D = ed^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

where  $e$  is the Napierian base,  $k$  is the Boltzmann constant,  $h$  is Planck's constant,  $Q$  is the activation energy for diffusion, and  $\Delta S^*$  the entropy of activation for diffusion. The term  $d$  is the distance between successive equilibrium positions of the diffusing particle and is of the order of a molecular diameter. From a plot of  $\log D$  against  $1/T$ , the activation energy  $Q$  can be evaluated. This has been done for water diffusing through  $n$ -hexadecane and 2,6,10,15, 19, 23-hexamethyl-tetracosane.<sup>5</sup> It can be assumed that the diffusion process for water through saturated hydrocarbon liquids is analogous to a unimolecular reaction so that  $\Delta S^* = 0$  and  $\exp(\Delta S^*/R)$  of eq 2 goes to unity. Equation 2 can then be rearranged so that

$$d = \sqrt{\frac{D \exp(Q/RT)h}{ekT}} \quad (3)$$

Using eq 3 and values of  $D$  and  $Q$  previously determined,<sup>5</sup> the molecular diameter of water was calculated. Table I compares results for water diameters based on eq 1 and 3.

A remarkably close agreement is seen to exist between the diameters determined from the water-hydro-

carbon systems up to  $n$ - $C_{16}$ . These diameters agree very well with some literature values: 2.50,<sup>6</sup> 2.64,<sup>6</sup> 2.78,<sup>7</sup> and 2.88 Å.<sup>6</sup> In a recent analysis of surface tension data for water,<sup>8</sup> the area of a surface water molecule was determined. From this, a molecular diameter of approximately 2.5 Å was determined.

The high value for the water diameter determined from the water-hexamethyltetracosane system is attributed to the six tertiary hydrogen atoms of the hydrocarbon molecule. The diffusing water molecule polarizes these atoms, resulting in a stronger solute-solvent interaction than in the normal hydrocarbon systems. Consequently, the assumption that  $\Delta S^* = 0$  for this system is not valid. In view of the different bases for eq 1 and 3, the close agreement between the molecular diameters of water determined from the hydrocarbon solvent systems up to  $n$ - $C_{16}$  is noteworthy.

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## A New Method for the Synthesis of Radical Cations of Aromatic Hydrocarbons<sup>1</sup>

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Radical cations of aromatic hydrocarbons have been produced and studied using electron spin resonance (esr) by a number of investigators employing several different procedures,<sup>2-12</sup> but many of the species are

**Table I:** Water Diameters,  $d$ , in Angstroms

Temp. °C	Eq 1 Water- $n$ -alkanes $C_7$ - $C_{16}$	Eq 3	
		Water- $n$ -hexadecane	Water- hexamethyl- tetracosane
25	2.74	2.77	4.52
40	2.72	2.69	4.41

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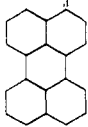
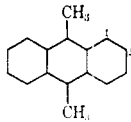
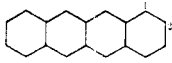
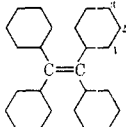
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Table I: Hyperfine Splitting Constants

Radical	Method <sup>a</sup>	Position	Hyperfine splitting, <sup>b</sup> gauss	Line width, <sup>c</sup> gauss
Perylene <sup>+</sup>				
	C	1	3.0562 ± 0.0012	0.040
		2	0.4466 ± 0.0006	
		3	4.0549 ± 0.0015	
9,10-Dimethylantracene <sup>+</sup>				
	C	1	2.4966 ± 0.0008 <sup>d</sup>	0.025
		2	1.2110 ± 0.0007 <sup>d</sup>	
		CH <sub>3</sub>	7.9582 ± 0.0013 <sup>d</sup>	
Tetracene <sup>+</sup>				
	C	1	1.6757 ± 0.0016	0.030
		2	1.0319 ± 0.0011	
		3	5.0791 ± 0.0020	
	E	1	1.6782 ± 0.0018	0.060
		2	1.0315 ± 0.0013	
		3	5.0294 ± 0.0021	
Tetraphenylethylene <sup>+</sup>				
	C	1	2.109 ± 0.010	0.025
		2	0.718 ± 0.010	
		3	2.976 ± 0.020	

<sup>a</sup> C: chemical preparation with CF<sub>3</sub>CO<sub>2</sub>H-CH<sub>3</sub>NO<sub>2</sub>; E: electrolytic preparation in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Absolute values of hyperfine splitting constants are given. All ring-proton splittings except position 2 in perylene are presumably negative, and the methyl-proton splittings are presumably positive. Errors are one standard deviation.<sup>7</sup> <sup>c</sup> Separation between extrema of the first derivative of each line in the spectrum. <sup>d</sup> Corrected for resolved second-order shifts.

rather unstable at room temperature. We have devised a chemical oxidation procedure by means of which stable radical cations with well-resolved esr spectra can be obtained from perylene, 9,10-dimethylantracene, tetracene, and tetraphenylethylene. The tetracene radical cation has also been prepared by electrolytic oxidation.

In the chemical procedure, 1 ml of trifluoroacetic acid is added under vacuum to 1 ml of a 0.001 *M* solution of the parent hydrocarbon in nitromethane. An esr spectrum is obtained immediately after the tube containing the frozen sample is sealed off and thawed.

Hydrocarbons whose oxidation half-wave potential<sup>13</sup> corresponds to less than 1.2 v (*vs.* Ag/AgClO<sub>4</sub> reference electrode) are oxidized by this method, whereas those whose potential is larger than 1.2 v are not. Recently, other investigators<sup>11,12</sup> have employed AlCl<sub>3</sub> in nitromethane or nitrobenzene to produce radical cations, but

we have found that more stable aromatic hydrocarbon radicals are produced with our procedure. The esr spectrometer and the method of analysis of spectra have been described elsewhere.<sup>7</sup>

The perylene cation radical has been investigated by several workers<sup>3,4,6,10,11,14</sup> and was found to be moderately stable. We have obtained a blue solution of the cation radical which is stable for several weeks

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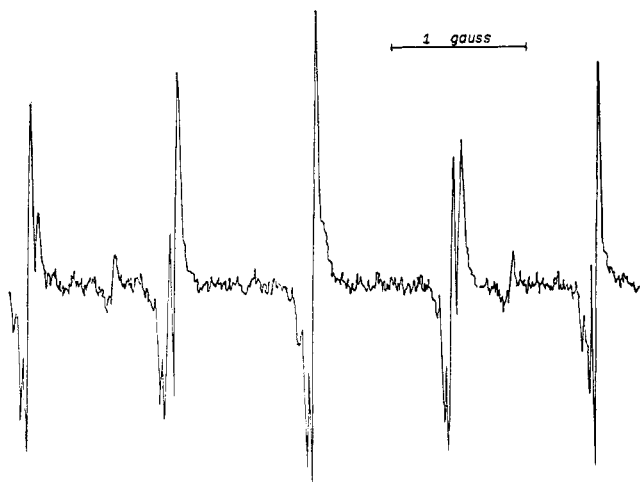


Figure 1. Central portion of the first derivative of the esr absorption signal from the 9,10-dimethylantracene cation radical, showing second-order splittings. The fine structure of the center line arises entirely from second-order effects, whereas that of the other lines arises also from first-order effects. The magnetic field increases to the right.

at room temperature and exhibits a strong, well-resolved (line widths of less than 0.040 gauss) esr spectrum. One hundred lines were detectable. The splitting constants (see Table I) are almost identical with those in sulfuric acid.<sup>14</sup>

A very well-resolved spectrum (line widths *ca.* 0.025 gauss) was obtained from a blue solution of the cation radical of 9,10-dimethylantracene that was stable for several days. The stability and resolution of spectra prepared in this way were superior to those reported previously.<sup>9-11</sup> Our results for the hyperfine splittings are in agreement with the earlier and less accurate data. Second-order components arising from the methyl-proton splitting were resolved in each line,<sup>15,16</sup> as can be seen from Figure 1, and appropriate corrections had to be applied.<sup>17</sup> Measurements of the positions of the major component of each line without applying second-order corrections gave:  $a_1 = 2.4892 \pm 0.0020$ ,  $a_2 = 1.2085 \pm 0.0015$ , and  $a_{\text{CH}_3} = 7.9522 \pm 0.0052$  gauss.

A well-resolved, complex (405 lines predicted) spectrum was obtained from the purple solution of the cation radical of tetraphenylethylene. It was stable for several days, while that obtained in  $\text{SbCl}_5\text{-CH}_2\text{Cl}_2$  at low temperatures was very unstable, and the radical has not been reported in  $\text{H}_2\text{SO}_4$ . Our splitting constants are in approximate agreement with the earlier<sup>10</sup> and less accurate results.

A strong, well-resolved spectrum of the tetracene cation radical was obtained from tetracene using the  $\text{CF}_3\text{COOH-CH}_3\text{NO}_2$  procedure. The solution was

orange and the radical was stable for several days. We have also generated this radical by vacuum electrolytic oxidation in  $\text{CH}_2\text{Cl}_2$ . A vacuum electrolytic cell similar to one described previously,<sup>7</sup> but employing a platinum anode and cathode, was used. The  $\text{CH}_2\text{Cl}_2$  solution was 0.1 *M* in supporting electrolyte (tetra-*n*-butylammonium perchlorate) and 0.005 *M* in tetracene. Electrolysis for 1 hr at a potential of 0.90 v (*vs.*  $\text{Ag}|\text{AgClO}_4$ ) and initial current of 1.5 ma yielded a brown solution of the cation radical. The esr spectrum was recorded at  $-61^\circ$ , since the signal was found to be quite unstable at room temperature. Electrolytic generation in  $\text{CH}_2\text{Cl}_2$  was found to be unsatisfactory for other species, and we are currently investigating different solvents for use in electrolysis. Tetracene has been produced in<sup>3,6,10,11</sup>  $\text{H}_2\text{SO}_4$  and in<sup>14</sup>  $\text{SO}_2\text{-BF}_3$ , and the color of the positive ion has been reported to be green. We have, as yet, no explanation for the color of the  $\text{CF}_3\text{COOH-CH}_3\text{NO}_2$  solution. The only other accurate results for tetracene were obtained in sulfuric acid<sup>18</sup> [ $a_1 = 1.690 \pm 0.002$ ,  $a_2 = 1.030 \pm 0.001$ ,  $a_3 = 5.056 \pm 0.003$ ] and in  $\text{SO}_2\text{-BF}_3$ <sup>14</sup> [ $a_1 = 1.694 \pm 0.002$ ,  $a_2 = 1.030 \pm 0.001$ ,  $a_3 = 5.061 \pm 0.001$ ]. These data, and those in the table, indicate that there is a slight solvent dependence of the splittings.

Further investigations on this and related systems are in progress.

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## Acetylene Production by the Radiolysis of Methane<sup>1a</sup>

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An especially disturbing aspect of the radiolysis of methane is the uncertainty as to whether acetylene is produced as a product. Hummel<sup>2</sup> has presented strong evidence from two separate experiments that acetylene

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