

Organized Monolayers of Polycyclic Aromatic Quinones

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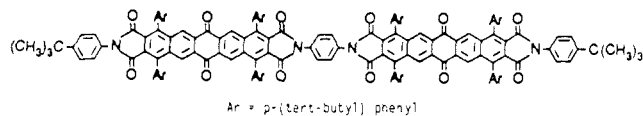
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Organized monolayers are of interest for a variety of scientific and technological applications. These systems could, for example, afford the realization of long envisioned molecular electronic devices¹ by providing structures with appropriate optical, electrical or redox characteristics. Studies of conventional amphiphiles (structural partitioning of hydrophilic/hydrophobic properties) have dominated the field of monolayer science, but modern synthetic techniques might provide a greatly increased range of materials for monolayer formation. In this context, the present study evolved from the development of a synthetic method for the production of some unusual, soluble polyacenequinone derivatives.² A particularly interesting example is **1**, a rod-like molecule 52.8



1

Å long. We have determined surface isotherms of **1** and similar compounds and report that they form organized monolayers at the air-water interface. These stiff, aromatic molecules pack "end-on" in compressed monolayers; they are oriented perpendicular to the water surface. This behavior is of special interest because these compounds are not amphiphiles in the traditional sense, i.e., having a separate hydrophobic group attached to a polar, hydrophilic region.³ These preliminary observations imply that a wide variety of polycyclic aromatics with specific functionalities and lengths can be prepared to form monolayers with some unique attributes.

Surface pressure isotherms were determined with a conventional Teflon Langmuir trough interfaced to a computer providing analogue-to-digital conversion and by using a Wilhelmy balance system. Chloroform was the spreading solvent in all cases. Compound **1** and several related structures, **2-6** shown in Table I, produced coherent, incompressible monolayers with breaking pressures in excess of 50 mN m⁻¹. All isotherms were of simple character, with no distinctive features. The apparent areas/molecule, as determined by extrapolation of the limiting slope of the surface pressure isotherm, are given in Table I. Also given are areas estimated from space filling CPK models. Compounds **1-6** are all derived from the same basic building unit, and their

Table I. Observed and Calculated Molecular Areas of Polycyclic Quinones

COMPOUND	STRUCTURE ^a	AREA/MOLECULE-Å ²	
		EXP.	CALC.
1	SEE TEXT	124	114
2		119	114
3		104	114
4		102	114
5		110	114
6		130	114
7		48	42
8		21	24
9		40	50
10		--	90
11		--	24
12		--	24
13		--	114
14		--	24
15		--	90

^a Ar = *p*-(*tert*-butyl)phenyl; Ph = phenyl. All compounds except **3**, **5**, **7**, **9**, and **12** have been previously reported. The new compounds were characterized spectroscopically and gave satisfactory elemental analyses and high resolution mass spectra. Details will be reported in a later publication.

projected, "end-on" areas must all be similar, about 114 Å².⁴ If the molecules were lying flat on the surface or on edge, the determined area for each compound would be different and not in agreement with estimates from models. For instance, compound **1** would provide areas of about 312 Å² or 988 Å² for "edge-on" or flat on the surface configurations, respectively. Preliminary study of simpler but related polycyclic aromatics revealed that compounds **7-9** also formed monolayers with apparent molecular

(4) Because the width and thickness vary along the length of each molecule, the minimum area at most dense packing can only be estimated. Using CPK models the common width and thickness for **1-6** were taken as 19 and 6 Å, respectively. These dimensions are determined by the Ar = *p*-*tert*-butylphenyl groups.

(1) Feynman, R. *Sat. Rev.* **1960**, 432, 45.(2) Christopfel, W. C.; Miller, L. L. *J. Org. Chem.* **1986**, 51, 4169. Kenny, P. W.; Miller, L. L. *Chem. Commun.* **1988**, 84. Chiba, T.; Kenny, P. W.; Miller, L. L. *J. Org. Chem.* **1987**, 52, 4327. Christopfel, W. C.; Miller, L. L. *Tetrahedron* **1987**, 43, 3681.(3) Nontraditional compounds which form coherent monolayers include the following: (a) Oligothiophenes: Schoeler, U.; Tews, K. H.; Kuhn, H. *J. Chem. Phys.* **1974**, 61, 5009. Yamamoto, N.; Tsubomura, H. *Thin Solid Films* **1980**, 68, 191. Nakayama, J.; Hoshino, N.; Fukuda, K. *Abstracts of Papers, Third International Conference on Langmuir-Blodgett Films*, Göttingen, FRG, 1987; p 174. (b) Polyphenyls: Daniel, M. F.; Lettington, O. C.; Small, S. M. *Thin Solid Films* **1983**, 99, 61. (c) Phthalocyanines: Roberts, G. G.; Petty, M. C.; Baker, S.; Fowler, M. T.; Thomas, N. J. *Thin Solid Films* **1985**, 132, 113. Kalina, D. A.; Crane, S. W.; *Thin Solid Films* **1985**, 134, 1098. Barger, W. R.; Snow, A. W.; Wohltjen, H. Y. Y.; Jarvis, N. L. *Thin Solid Films* **1985**, 133, 197. Aroca, R.; Jennings, C.; Kovacs, G. J.; Loutfy, R. O.; Vincett, P. S. *J. Phys. Chem.* **1985**, 89, 4051. Kim, J.-H.; Cotton, T. M.; Uphaus, R. A. *Abstracts of Papers, Third International Conference on Langmuir-Blodgett Films*, Göttingen, FRG 1987; p 50.

areas consistent with an end-on, upright orientation. The six compounds **10–15** showed no evidence of monolayer formation. These shorter compounds have only four or five fused rings and only nominal hydrophilic character (in the case of **15**, no hydrophilicity). They are included to indicate the relationship between structure- and monolayer-forming ability,⁵ and their behavior stands in contrast to that of the other compounds studied. The compounds which do form stable monolayers possess extensive ring systems which enhance film-forming capacity through cohesive interaction of the aromatic moieties. End-on packing maximizes interaction between the molecular surfaces and minimizes contact of the hydrophobic molecular surfaces with the water surface.

The present results indicate that the extended, rigid systems described here may be of considerable value in the construction of a variety of functional multilayer systems formed by the Langmuir–Blodgett transfer technique. Quinones are essential elements of any biomimetic model based on the photosynthetic reaction center as well as for other electron transfer model systems and electrochemical studies. Additionally, these very long, stiff molecules of accurately known length possessing extended π -bonded systems provide unusual possibilities for optical and electronic properties in monolayer assemblies.

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(5) Stearyl anthraquinones form oriented monolayers: Nahara, K.; Fukuda, K. *J. Coll. Interfac. Sci.* **1981**, *83*, 401.

An ESR Investigation of the Structure and Rearrangement of the Hexamethyl(Dewar benzene) Radical Cation

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Despite the much greater thermodynamic stability of hexamethylbenzene (HMB) over its strained "Dewar" isomer (HMD), the thermal conversion of HMD to HMB proceeds with an activation energy of 37 kcal/mol;^{1,2} this has been partly ascribed to the orbital symmetry forbidden nature of the process.³ In contrast, photosensitized conversion of HMD to HMB is well-known.⁴

The mechanism proposed for this reaction involves the transfer of an electron from HMD to the photosensitizer with the formation of HMD^{•+} radical cations.² Since this mechanism requires a very facile rearrangement of HMD^{•+} to HMB^{•+}, it has been questioned whether HMD^{•+} can be an energy minimum. A laser-flash spectroscopic study has recently shown the presence of only the HMB^{•+} cation, indicating that the lifetime of the HMD^{•+} cation must be less than 15 ns.⁵

In order to study the structure and stability of this elusive HMD^{•+} cation, we used the now well established method of exposing dilute frozen solutions of substrates in freon solvents to ionizing radiation.^{6,7} This technique often gives well-resolved ESR spectra of the corresponding substrate radical cations, following what is essentially a single electron oxidation by CFCl₃^{•+} cations, and is applicable to substrates with ionization potentials of <11.8 eV.

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- (2) Adam, W.; Chang, J. C. *Int. J. Chem. Kinet.* **1969**, *1*, 487.
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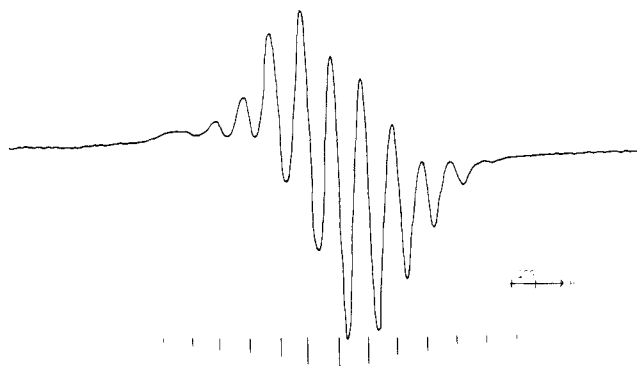


Figure 1. ESR spectrum of hexamethyl(Dewar benzene) radical cations (HMD)^{•+} in a CFCl₃ matrix at 77 K.

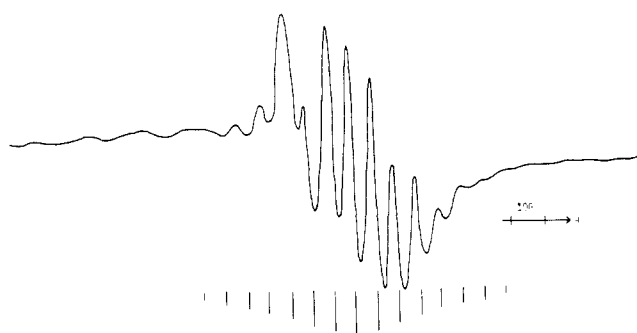
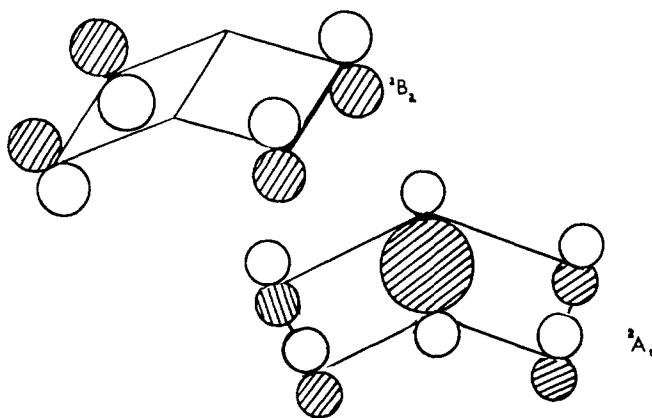


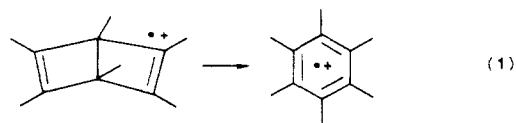
Figure 2. ESR spectrum recorded at 150 K, showing features assigned to hexamethylbenzene radical cations (HMB)^{•+} formed by ring opening of HMD^{•+} cations.

Chart I



The spectrum obtained from HMD is shown in Figure 1. This comprises a set of 13 lines with nearly binomial intensities and a single splitting of 9.5 G, indicating hyperfine coupling to four equivalent methyl groups. This must be due to the HMD^{•+} radical cation, which is *stable* in the CFCl₃ matrix.

On annealing the sample to ca. 150 K, the spectrum suddenly changed to that shown in Figure 2. We interpret this in terms of a rearrangement of the HMD^{•+} cation to its more stable isomer, HMB^{•+} (eq 1). This is confirmed by the observation of an



identical spectrum from an authentic sample of HMB. The coupling of 6.7 G is virtually identical with that previously observed for HMB^{•+} cations in a sulfuric acid solution.⁸ On recooling either sample containing HMB^{•+} cations to 77 K, the spectrum

(8) Hulme, R.; Symons, M. C. R. *J. Chem. Soc.* **1965**, 1220.