of 88.9% d_4, 9.6% d_3, and 0.8% d_2 as determined by mass spectrometry.

2,6,6-d_3-Methylcyclohexene was prepared by the methyl Grignard dehydration sequence described above except an excess of Grignard reagent was used. The product, obtained in 37% yield, had isotopic composition 89% d_3, 10% d_2, and 1% d_0 after collection from a gas chromatographic column.

4,4-d_2-Methylcyclohexene.—Methylcyclohexen-4-one was prepared following the procedure of Braude and Webb.[14] Reduction of 2.86 g (0.026 mole) of methylcyclohexen-4-one with 0.25 g (0.007 mole) of lithium aluminum deuteride in 15 ml of anhydrous ether produced 2.5 g (83% yield) of crude methylcyclohexen-4-d_1-4-ol. The alcohol (0.022 mole) was dissolved in 20 ml of pyridine. The solution was cooled to 5° in an ice bath and 5 g (0.044 mole) of mesyl chloride dissolved in 10 ml of pyridine was added with stirring at such a rate that the solution remained below 10°. After storing the reaction mixture in a refrigerator overnight, water was added to it and two layers were separated. The aqueous layer was extracted with ether and the combined ether layers were washed many times with water. Crude mesylate (3.13 g, 74% yield) was obtained as an oil upon removal of the solvent.

The displacement of the mesylate was effected by treatment with 0.30 g (0.0072 mole) of lithium aluminum deuteride in 40 ml of anhydrous ether at 35° for 30 hr. The olefin, along with some ether, was removed from unreacted mesylate by distillation at low pressure and collected in a liquid nitrogen cooled trap. Final purification was effected by collection from a gas chromatographic column. The nuclear magnetic resonance spectrum indicated essentially quantitative deuteration. The mass spectrum indicated a deuterium incorporation of 96% d_2, 3% d_1, and 1% d_2. The contamination of the sample with a few per cent of monodeuteriomethylcyclohexadiene was obvious from this mass spectrum.

2,2,6,6-d_4-Methylenecyclohexane.—All glassware was oven dried. The dimethyl sulfoxide was dried over calcium hydride for 2 days and distilled into a flask containing type 4A molecular sieve.

Sodium hydride (1.4 g of a 55% dispersion in mineral oil, 0.0325 mole) was placed in a three-necked flask fitted with a condenser, nitrogen inlet, and dropping funnel. The flask was evacuated twice and filled each time with nitrogen. After the second flushing, nitrogen was passed continuously through the system. Dimethyl sulfoxide (12.5 ml) was added and the flask was heated to 75° and this temperature was maintained until the reaction was complete (approximately 50 min). The green-gray solution was cooled with an ice bath and 21.8 g (0.06 mole) of triphenylmethylphosphonium bromide dissolved in 50 ml of warm dimethyl sulfoxide was added with stirring. The reaction mixture became orange upon initial addition and dark yellow-green upon further addition. The reaction mixture was stirred for 15 min and 2.8 g (0.0285 mole) of 2,2,6,6-d_4-cyclohexanone (90% d_4) was added slowly, a slight exothermicity being noted. The solution was stirred for 40 min and all volatile compounds were immediatedly removed from the dimethyl sulfoxide at low pressures, 2.5 g (89% yield) of crude product being collected in a liquid nitrogen cooled trap. The pure olefin, after collection from a gas chromatograph, was shown by mass spectrometry to be 90% d_4.

7,7-d_2-Methylenecyclohexane was obtained in 30% over-all yield from pyrolysis at 505–510° of cyclohexane-d_2-carbinyl acetate, itself available by acetylation of the reduction product of methyl cyclohexanecarboxylate by lithium aluminum deuteride. A nuclear magnetic resonance spectrum of material purified by gas chromatography indicated quantitative deuteration. Its mass spectrum indicated greater than 98% d_2.

Registry No.—**3**, 591-49-1; **4**, 7721-69-9; **5**, 7721-70-2; **6**, 7721-71-3; **7**, 1192-37-6; **8**, 1560-57-2; 2,2,6,6-d_4-methylenecyclohexane, 3452-02-6; 2,2,6,6-d_4-cyclohexanone, 1006-03-7.

Acknowledgments.—This research was supported in part by grants from the Petroleum Research Fund (administered by the American Chemical Society) and the Research Corp.

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[14] A. Braude, A. A. Webb, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

Oxidation, Reduction, and Electrochemiluminescence of Donor-Substituted Polycyclic Aromatic Hydrocarbons[1]

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The effect of chemical structure on electrochemiluminescence (ECL) and the molecular properties associated with this phenomenon have been explored. Polarographic oxidation and reduction potentials and the fluorescence emission spectra in aprotic media of donor-substituted polycyclic aromatic molecules were measured. The stabilities of ion radicals generated from these compounds were determined by means of cyclic voltammetry. The results are in general agreement with the assumption that the efficiency of the ECL process is associated with the fluorescence, efficiency, and stability of the one-electron oxidation and reduction products under the experimental conditions. While multiple donor substituents on polycyclic aromatic nuclei result in fluorescent compounds with stable cations, the orientation of such substituents which is most effective in stabilizing the cation also results in extensive anion destabilization. The results are discussed in terms of molecular orbital theory.

The recent finding that successive chemical or electrochemical reduction and oxidation of fluorescent aromatic hydrocarbons in aprotic solvents where excess energy is available results in luminescent emission[2] (electrochemiluminescence or ECL) prompted our examination of other molecules which might exhibit this behavior. The usually fluorescent polycyclic aromatic hydrocarbons form stable anion radicals and unstable cation radicals in N,N-dimethylformamide (DMF). If it is assumed that anion–cation annihilation is an intermediate step in the ECL process, then cation stabilization should result in improved ECL efficiency. One way in which cation stabilization could be achieved is through multiple electron-donor substituents. While qualitative considerations suggest that such substituents would exert a deleterious effect on fluorescence efficiency and anion-radical stability, quantitative evaluations of such effects have not been made. The advantages of cation-radical stabilization could outweigh these destabilizing factors in the over-all ECL

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[1] Cumulative Influence of Substituents on the π-Electron Properties of Aromatic Systems. XI.

[2] *Cf.* A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, **88**, 2864 (1966), and references therein.

process. The effect of donor substitution on the polarographic half-wave potentials of polycyclic hydrocarbons was also of interest. One might anticipate a rough linear-free-energy change relationship of half-wave potentials with ion-radical reactivities in series of similar compounds.

This experimental investigation was undertaken to evaluate the effect of the number and position of various donor substituents in polycyclic hydrocarbons on their performance as ECL emitters, on half-wave oxidation and reduction potentials, and on ion-radical stability and fluorescence which may be related physical properties. The effect of methoxy, methylthio, and dimethylamino groups on the naphthalene, anthracene, biphenyl, and pyrene nuclei were examined in particular detail.

Results

Preparation of Compounds.—The commercially available compounds and those prepared through routine synthesis are described in the Experimental Section. Preparation of 1,4,5,8-tetramethoxynaphthalene[3] was achieved by treatment of 1,5-dibromo-4,8-dimethoxynaphthalene[4] with sodium methoxide in DMF.

1,5-Dimethoxy-4,8-bis(methylthio)naphthalene and 1,5-dimethoxy-4,8-diphenoxynaphthalene were also prepared from 1,5-dibromo-4,8-dimethoxynaphthalene, employing cuprous methylmercaptide[5] and potassium phenoxide, respectively, in displacement reactions. 9,10-Dibromoanthracene was treated similarly to afford 9,10-bis(methylthio)anthracene and 9,10-diphenoxyanthracene.

The two planar bisdimethylaminonaphthalenes (2,6 and 2,7) are unknown in the literature as is 1,6-bisdimethylaminopyrene. All three were readily prepared by alkylation of the corresponding diamines. The six symmetrical bis(methylthio)naphthalenes, 1,6-bis(methylthio)pyrene, and three bis(methylthio)biphenyls were prepared either from the corresponding sulfonic acids which were converted to the sulfonyl chlorides, reduced to the mercaptans, and then methylated, or from the corresponding dibromo derivatives which underwent substitution when treated with cuprous methyl mercaptide. Although the latter reaction often proceeds in poor yield from different polybromo aromatics, a workable amount of the pure multiple methylthio-substituted aromatic hydrocarbon was always obtained. On the other hand, the procedures involving reduction of arylsulfonyl chlorides which give high yields of mercaptans in some instances may give no desired product at all in what would appear to be analogous circumstances with other isomers. Similar difficulties with this reduction are known in the literature.[5,6]

Measurements.—In Table I are reported polarographic and fluorescence data for the substituted polycyclic aromatic hydrocarbons examined in this investigation. Polarographic half-wave oxidation potentials were taken at a rotating platinum electrode in acetonitrile (AN) while the half-wave reduction potentials were measured at a dropping mercury electrode (DME) in dimethylformamide (DMF) solution so that the results could be directly comparable to literature data.[7,8] Oxidation curves in DMF and reduction curves in AN were also run in some instances. The data are reported in only one solvent for either oxidation or reduction so that the effects of the patterns of substitution can be more accurately ascertained. In general, there is several hundredths of a volt difference in half-wave potentials for the same process intensity of ECL emission in these instances.

Table I

Polarographic and Fluorescence Data for Donor-Substituted Polycyclic Aromatic Hydrocarbons

Name	$E_{1/2}$ (oxidn) (CH_3CN), v[a]	$E_{1/2}$ (redn) (DMF), v[a]	Soln fluorescence
1-Methoxynaphthalene	+1.38	−2.65	Wk blue
2-Methoxynaphthalene	+1.52	−2.60	Wk blue
1,3-Dimethoxynaphthalene	$+1.26^5$	−2.61	Nil
1,4-Dimethoxynaphthalene	+1.10	−2.69	Blue
1,5-Dimethoxynaphthalene	+1.28	-2.75^5	Nil
1,6-Dimethoxynaphthalene	+1.28	−2.68	Nil
1,7-Dimethoxynaphthalene	+1.28	−2.67	Nil
1,8-Dimethoxynaphthalene	+1.17	−2.72	Nil
2,3-Dimethoxynaphthalene	+1.39	−2.73	Nil
2,6-Dimethoxynaphthalene	+1.33	−2.60	Wk blue
2,7-Dimethoxynaphthalene	+1.47	−2.68	Wk blue
1,4,5,8-Tetramethoxynaphthalene	+0.70	−2.69	Wk blue
1-Dimethylaminonaphthalene	+0.75	−2.58	Blue
1,5-Bis(dimethylamino)-naphthalene	$+0.58^5$	−2.64	Blue
2-Dimethylaminonaphthalene	+0.67	-2.63^5	Blue
2,6-Bis(dimethylamino)-naphthalene	+0.26	−2.71	Blue
2,7-Bis(dimethylamino)-naphthalene	+0.57	−2.77	Blue
1-(Methylthio)naphthalene	+1.32	−2.25	Nil
2-(Methylthio)naphthalene	$+1.36^5$	−2.28	Wk blue
1,4-Bis(methylthio)naphthalene	+1.07	−2.10	Purple
1,5-Bis(methylthio)naphthalene	$+1.26^5$	−2.15	Nil
1,8-Bis(methylthio)naphthalene	+1.09	−2.22	Nil
2,3-Bis(methylthio)naphthalene	$+1.35^5$	−2.21	Nil
2,6-Bis(methylthio)naphthalene	+1.10	−2.24	Purple
2,7-Bis(methylthio)naphthalene	+1.33	−2.25	Nil
1,4,5,8-Tetraphenylnaphthalene	+1.39	−1.98	Blue
1,5-Dimethoxy-4,8-bis(methylthio)naphthalene	+0.70	−2.42	Wk blue
1,5-Dimethoxy-4,8-diphenoxy-naphthalene	+0.98	−2.47	Wk blue
9-Methoxyanthracene	+1.05	−1.92	Blue
9,10-Dimethoxyanthracene	+0.98	−1.90	Blue
9,10-Bis(methylthio)anthracene	+1.11	−1.55	Green
9,10-Bis(2,6-dimethoxyphenyl)-anthracene	+1.18	−2.08	Blue
9,10-Bis(phenylethynyl)-anthracene	$+1.16^5$	−1.29	Yellow-green
9,10-Diphenoxyanthracene	+1.20	−1.71	Blue
4-Methoxybiphenyl	+1.53	−2.73	Nil
4,4′-Dimethoxybiphenyl	+1.30	Not red	Nil
3,3′-Dimethoxybiphenyl	+1.60	−2.54	Nil
2,2′-Dimethoxybiphenyl	+1.51	Not red	Nil
4,4′-Bis(methylthio)biphenyl	$+1.25^5$	−2.29	Nil
3,3′-Bis(methylthio)biphenyl	$+1.47^5$	−2.35	Nil
2,2′-Bis(methylthio)biphenyl	+1.39	−2.58	Nil
N,N′-Tetramethylbenzidine	+0.43	Not red	Blue
10,10′-Dimethoxy-9,9′-bianthracenyl	+1.10	−1.80	Blue
1,6-Bis(dimethylamino)pyrene	+0.49	−2.16	Blue-green
1,6-Dimethoxypyrene	+0.82	−2.19	Wk blue
1,6-Bis(methylthio)pyrene	+0.96	−1.83	Blue

[a] Measured *vs.* SCE.

Since ECL emission is frequently found to be identical with that of the normal fluorescence emission of the

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[3] K. Zahn and P. Ochwat, *Ann.*, **462**, 83 (1928); W. H. Perkin, Jr., and C. Weizmann, *J. Chem. Soc.*, **89**, 1658 (1906).

[4] A. H. Carter, E. Race, and F. M. Rowe, *ibid.*, 236 (1942).

[5] A. Zweig and J. H. Lehnsen, *J. Am. Chem. Soc.*, **87**, 2647 (1965).

[6] C. S. Marvel and P. D. Caesar, *ibid.*, **73**, 1098 (1951); C. G. Overberger, H. Biletch, and F. W. Orttung, *J. Org. Chem.*, **24**, 290 (1959).

[7] E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963); H. Lund, *Acta. Chem. Scand.*, **11**, 1323 (1957).

[8] A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

TABLE II

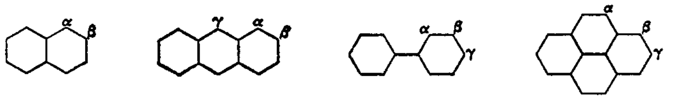
CYCLIC VOLTAMMETRY AND EMISSION CHARACTERISTICS OF DONOR-SUBSTITUTED POLYCYCLIC AROMATICS IN DMF

Compd	Radical stability, sec		Emission	Max, mμ	Fluorescence efficiency
	Cation	Anion	ECL	(fluorescence)	
1,4-Dimethoxynaphthalene	0.2	0.01	560	460	0.57
9-Methoxyanthracene	0.01	15	*a*	420	...
9,10-Dimethoxyanthracene	0.01	15	*a*	435	...
9,10-Bis(2,6-dimethoxyphenyl)anthracene	15	15	425[b]	425[b]	0.78
10,10′-Dimethoxy-9,9′-bianthracenyl	0.01	15	...	502	...
9,10-Diphenoxyanthracene	0.01	15	...	432	...
1,4-Bis(methylthio)naphthalene	0.2	0.01	...	405	...
2,6-Bis(methylthio)naphthalene	...	...	...	402[c]	...
9,10-Bis(methylthio)anthracene	...	...	...	467	...
1-Dimethylaminonaphthalene	*d*	9–10	465	435	...
2-Dimethylaminonaphthalene	0.09	15	*a*	415	...
1,5-Bisdimethylaminonaphthalene	0.07	4	...	402	0.29
2,6-Bisdimethylaminonaphthalene	15	4–5	450–455	450–455	0.48
2,7-Bisdimethylaminonaphthalene	0.01	15	*a*	400–425	...
N,N′-Tetramethylbenzidine	15	Not red	*a*	403	...
1,6-Bisdimethylaminopyrene	15	2–3	545	453	0.60
1,4,5,8-Tetraphenylnaphthalene	...	...	430–440	430–440	...
9,10-Bis(phenylethynyl)anthracene	0.01	15	...	508 487	...
1,6-Bis(methylthio)pyrene	0.03	15	550	438 416	0.32

[a] Too brief and/or dim for quantitative study. [b] Less intense maxima at 405 and 450 mμ also recorded. [c] Less intense maxima at 389 mμ also recorded. [d] Coats the electrode.

TABLE III

POLAROGRAPHY AND HMO–HFMO COEFFICIENTS OF SOME POLYCYCLIC AROMATIC HYDROCARBONS



Compd	$E_{1/2}$ (oxidn) (CH_2CN), v[a]	$E_{1/2}$ (redn) (DMF), v[a]	Coefficients of HFMO position		
			α	β	γ
Naphthalene	+1.54	−2.54	0.425	0.263	...
Anthracene	+1.09	−1.96	0.311	0.220	0.440
Biphenyl	+1.78	−2.60	0.299	0.140	0.389
Pyrene	+1.16	−2.08	0.296	0.368	0

[a] Reference 7. [b] Reference 8.

neutral compound, the fluorescence efficiency (*i.e.*, the proportion of excited molecules which decay to the ground state with emission) must directly influence the intensity of ECL emission in these instances.

Qualitatively as indicated in Table I, only 19 of the 46 compounds showed moderate to strong visible fluorescence under solution conditions approximately those required for ECL study.

The ECL cell used in these studies consisted of two 1-cm² 80 mesh platinum gauze electrodes spaced 2 mm apart. The 19 moderately and strongly fluorescent compounds were examined as 10^{-3} *M* solutions in a conducting medium consisting of 0.1 *M* tetra-*n*-butylammonium perchlorate in dry, deaerated DMF. Using a line voltage transformer, 3–10 v rms (root mean square) at 60 cps was applied across the electrodes. No emission was detectable in the absence of a fluorescer. However, under these conditions, *all* of the 19 compounds electrochemiluminesced. In the instances where the emission was sufficiently intense, spectra were obtained. The fluorescence spectra of these molecules in DMF solution were also obtained. Stabilities of the cation and anion radicals were measured by cyclic voltammetry and the radical-ion lifetimes were estimated by scanning the cyclic voltammogram at varying speeds. In several instances the fluorescence efficiency of the compound at 10^{-3} *M* concentration in DMF was measured quantitatively in a calibrated cell. These data are summarized in Table II.

Discussion

The combined requirements of anion and cation stability and high fluorescence efficiency drastically limits the types of organic molecules suitable for use in the study of the ECL phenomenom. To these we must add solubility and chemical stability in the presence of electrodes, electrolyte, and solvent, and also photochemical stability.

As anticipated, the donor substituents sharply lower the oxidation potentials of polynuclear aromatic hydrocarbons. The extent of this effect is determined by the character of the groups as well as their number and positions and also by steric influences.[5] First-order perturbation theory predicts that donor substituents will raise the energy of the highest filled molecular orbital (HFMO) of the hydrocarbon (and thus ease its oxidation) to a greater extent when they are attached to a position of higher HFMO electron density.

Thus, as there can be seen from the coefficients which are reported in Table III, substitution at the α positions of naphthalene and the γ positions in biphenyl should exert the strongest influence on their oxidation potentials. Comparison of the oxidation potentials in Tables I and III shows that this is verified except for dimethylamino-substituted naphthalenes where steric hinderence in the α-substituted compounds results in reversal of the normal α,β relationship. It is worth noting, however, that a single, hindered dimethylamino group on an α-naphthyl position has about the same effect on the oxidation potential as four unhindered methoxy groups which cover all the α sites on 1,4,5,8-tetramethoxynaphthalene. Simple MO theory predicts that donor substitution at the 1,4 and the 2,6 positions will raise the HFMO further than similar substitution at the 1,5 and 2,7 positions, respectively, and this is also found experimentally. As shown in Figure 1, however, a selected set of Hückel heteroatom parameters[5] did not result in a remarkably good linear relationship between HFMO energies and oxidations potential for the 24 unhindered naphthalene derivatives. The heteroatom parameters used are reported in Figure 1, employing conventional[9] representations for heteroatom parameters ($\alpha_x = \alpha_c + h_x\beta_{cc}$ and $\beta_{cx} = k_{cx}\beta_{cc}$). The least-squares equation shown by the line in Figure 1 is $E_{1/2}$ (oxidn) $= -2.543(\alpha - E_{\text{HFMO}}/\beta) + 0.1066$ with a standard error of 0.0975 v, about twice that obtained for a similar series of benzene derivatives.[5] The results might be improved by further refinement of the heteroatom parameters, but there are also limits imposed by the basic inadequacy of the HMO method in evaluating interring interactions.

Steric hindrance to coplanarity would prevent most donor substituents from exerting a large effect on the HFMO energy if the substituents were on the 9 or 9,10 positions of anthracene even though the coefficient of the HFMO of anthracene is highest at these positions. As seen from the two methoxy derivatives however, the small influence at these positions is cumulative and thus may be ascribed to a weak resonance interaction. The phenylethynyl substituents at the 9,10-anthracene positions should not suffer steric hindrance; however, the relative electronegatively of sp-hybridized carbon makes this group behave as an electron acceptor rather than as a donor and this is reflected in the greater ease of reduction and difficulty of oxidation of 9,10-bisphenylethynylanthracene relative to anthracene. The compound was included in the study because of the expected lack of steric influence and also because of its very strong visible fluorescence.[10]

The oxidation potential data while interesting and necessary for the ECL study do not provide information regarding the stability of the one-electron oxidation product under the condition found in the ECL cell. The trend of such stabilities can be seen in the cyclic voltammetry data reported in Table II.

The stabilities of the three bisdimethylaminophthalene cation radicals reported in Table II are a further illustration of Michaelis[11] conclusions on the importance of both resonance delocalization and coplanarity in cation-radical stability. Of the three, only the 2,6 isomer allows both objectives and this shows the best cation stability. Steric hindrance at an α-naphthyl position clearly decreases stability relative to the unhindered β-naphthyl position. Some resonance stabilization and cation stability remain in the α-dimethylamino-substituted compound, however, and, if the π system conjugation is further extended as in 1,6-bisdimethylaminopyrene, the resulting cation is quite stable (lifetime, >15 sec).

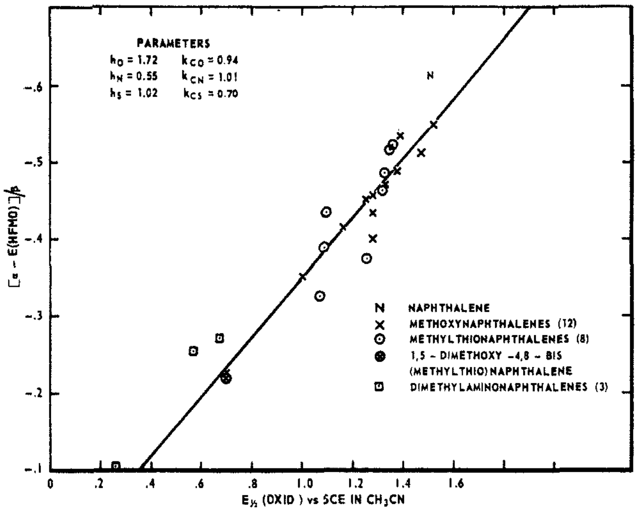


Figure 1.—Plot of HFMO energies of donor-substituted naphthalenes *vs.* polarographic oxidation potentials.

The reduction potentials of donor-substituted polycyclic aromatics are less influenced by the number and position of the substituent than the oxidation potentials. As seen from Tables I and III the dimethylamino- and methoxy-substituted naphthalenes all undergo one-electron reduction (as indicated by the diffusion currents) at potentials up to 0.2 v more negative than that required for reduction of naphthalene. The methylthio-substituted polycyclic compounds, however, reduce more readily than their parent hydrocarbons with diffusion currents indicative of two-electron reduction, except for 1,6-bis(methylthio)pyrene.

One-electron reduction of methoxy-substituted aromatics is thought to be the first step in the Birch reduction[12] employing alkali metals and amines; however, reduction of these compounds in aprotic media has not been extensively studied. The Birch reduction is sometimes accompanied by loss of a methoxy group. Such reductive cleavages have, for example, been reported in a study of dimethoxynaphthalene.[13]

While reductive cleavage with alkali metals in liquid ammonia is one of several observed reaction paths for aryl ethers it is the only reaction observed on treatment of alkyl aryl sulfides under these conditions.[14] Even in aprotic solvents such as 1,2-dimethoxyethane,[15] the action of alkali metals on phenyl sulfides results in reductive cleavage. The latter studies however were not carried over to polycyclic aromatic derivatives. Reductive cleavage probably involves addition of an electron to the antibonding orbital of a CS σ bond, and the energy of the orbital may be expected to remain essentially constant in a series of alkyl aryl sulfides. Lowering of the energy of the lowest unfilled MO

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[9] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemist," John Wiley and Sons, Inc., New York, N. Y., 1961.

[10] W. Reid, W. Donner, and W. Schlegelmilch, *Ber.*, **94**, 1051 (1961). We wish to thank A. Kende for bringing this compound to our attention.

[11] L. Michaelis, M. P. Shubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

[12] *Cf.* H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

[13] *Cf.* B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **29**, 2102 (1964).

[14] W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

[15] R. Gerdil and E. A. C. Lucken, *J. Chem. Soc.*, 3916 (1964).

(LUMO) of the π system by extending conjugation may therefore result in the π-LUMO being of lower energy than the antibonding CS σ orbital. If this occurred, then one-electron reduction of such sulfides could occur reversibly and without cleavage. The finding that *p*-carbethoxyphenyl phenyl sulfide is *not* cleaved with lithium[14] can be explained on this basis since the strongly electron-accepting carbethoxy group sharply lowers the lowest unfilled π molecular orbital. The two-electron reduction of 9,10-bis(methylthio)anthracene at an exceptionally low potential can be ascribed to weakening of the CS bonds resulting from the steric strain of the *ortho,ortho'* substitution. One-electron transfer is, however, clearly indicated in the first reduction step for 1,6-bis(methylthio)pyrene in DMF, which has an I_D value of 2.37.

Few reductive studies of N,N-dimethylamino-substituted aromatics have been made; however, it has been predicted[16] that a given carbon–nitrogen bond of this type should be cleaved reductively with greater difficulty than its carbon–oxygen analog. The results of studies of the alkali metal–ammonia reduction of N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine agree with this prediction since the primary products obtained show reduction of the benzene ring without disturbing the functional groups.[17]

A seemingly consistent inverse relationship between molecular cation and anion stabilities in DMF is seen in the results of the cyclic voltammetric investigations of 2,6- and 2,7-bisdimethylaminonaphthalene. As the aforementioned anion-radical cleavage mechanism could be responsible for the relative instability of the reduction product of 2,6-bisdimethylaminonaphthalene the CN π-bond orders of the filled and lowest unfilled molecular orbitals of the 2,6 and 2,7 isomers were examined. The 2,6 isomer was found to have a larger CN bond order in the neutral molecule (0.262 *vs.* 0.251) and smaller antibonding character in the lowest unfilled molecular orbital (-0.040 *vs.* -0.16), than the 2,7 isomer. This is not in accord with the proposed mechanism, and Nishimoto and Fumishiro[18] reported similar values of these bond orders in similar calculations on 2,6- and 2,7-naphthalenediol. Thus the molecular orbital calculations indicate that cleavage of the CN bond is *not* responsible for the decomposition of these anion radicals.[19]

The dimethylamino-substituted polycyclic aromatics were all found to be soluble in DMF and highly fluorescent and all electrochemiluminesced brightly for at least several minutes under the conditions described. Under standardized conditions, the brightest and longest lasting ECL emission was obtained from 2,6-bisdimethylaminonaphthalene. This was anticipated from the ion-radical lifetimes and serves to demonstrate the importance of both stable anions and cations for effective ECL emission.

The emission from 1,6-bisdimethylaminopyrene, although long lasting (~30 min), was very dim and at longer wavelength than the normal fluorescence emission. Eximer emission from pyrene is well known;[20] however, no evidence for such emission by ultraviolet excitation of the bisdimethylamino derivative could be detected in the solid or even at 0.05 M concentration in DMF. The 1,6-bis(methylthio) derivative of pyrene on the other hand was found to emit green in the solid (fluorescence $\lambda_{\max}$ 515 mμ) but its dim ECL emission (~550 mμ) did not correspond to this band.

Experimental Section[21]

Synthetic. 1-Methoxynaphthalene and 2-Methoxynaphthalene.—These compounds were Eastman Kodak Co. materials purified by distillation and recrystallization, respectively, before use. The nine dimethoxynaphthalenes were all prepared by treatment of the commercially available diols with dimethyl sulfate and sodium hydroxide and purified by distillation or recrystallization as applicable. The melting or boiling points of these materials corresponded to their literature descriptions.[22] Because of difficultly removed impurities in commercial 1,3-dihydroxynaphthalene, preparative-scale glpc purification of the crude methylated product was used (10-ft QF-1 column at 285°) to isolate the desired compound with a purity >99%. The crude methylated product contained 69.5% of 1,3-dimethoxynaphthalene, 23.4% of a second component, and small (1–4%) percentages of three unidentified materials. The nmr spectrum of the 23.4% component established it to be a nuclear methylated 1,3-dimethoxynaphthalene. The chemical shift of the single, unsplit aryl proton in this material (τ 3.50, 5 M in CCl_4) suggests that this compound is 4-methyl-1,3-dimethoxynaphthalene.

1-Methylthionaphthalene.—Cuprous methylmercaptide was prepared *in situ* from 44 g of cuprous chloride and excess (100 g) methanethiol. Excess methanethiol was removed in a stream of nitrogen (a strong, forced-draft hood is recommended) and 41.4 g (0.2 moles) of 1-bromonaphthalene (Eastman Kodak Co.) was added together with 125 ml of quinoline and 40 ml of pyridine. The mixture was heated and refluxed for 5 hr, then cooled to ambient temperature and poured into excess ice and hydrochloric acid and allowed to stand overnight. The product was filtered and the filtrate was extracted with two 200-ml portions of ether and 100 ml of benzene. The filtered solid was triturated with ether and benzene. The extracts were combined and washed with 10% hydrochloric acid, water, concentrated ammonium hydroxide, and water. Drying over sodium sulfate, concentration, and distillation at 1 mm gave 7.9 g (~26%) of 1-methylthionaphthalene, bp 120–145°. The nmr spectrum of this material showed a methyl to aryl proton ratio of 3:7.7 (theoretical 3:7). Redistillation gave 5.37 g at 118–122° (1 mm) with a purity of 98% by vpc (6-ft Qr column at 210°). A 1.7% impurity was found with a retention time of 1.09 relative to the major product. Dissolution of the 98% pure 1-methylthionaphthalene in concentrated H_2SO_4 gave an esr spectrum identical with that of the cation radical of 1,4-bis(methylthio)naphthalene,[23] suggesting that the latter is the major impurity in 1-methylthionaphthalene, and that 1,4-dibromonaphthalene is present to approximately the same extent in 1-bromonaphthalene.

2-Methylthionaphthalene.—Treatment of 10.0 g (0.063 mole) of 2-naphthalenethiol (Eastman Kodak Co.) with 20 g (0.16 moles) of dimethylsulfate, and 50 ml of methanol with a solution of 10 g of sodium hydroxide in 30 ml of water gave, after 1 hr of reflux and cooling, a white solid. This was filtered, washed with water, dried, and recrystallized from ethanol to give 6.3 g (52%) of desired product, mp 59–60° (lit.[24] 60–61°).

1,4-Bis(methylthio)naphthalene, and 2,3-Bis(methylthio)naphthalene.—These compounds were prepared from 1,4-dibromonaphthalene (Eastman Chemical Co.), 2,3-dibromonaphthalene (K & K Laboratories), and cuprous methylmercaptide in a

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[16] H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1962, p 184.

[17] B. B. Millward, *J. Chem. Soc.*, 26 (1960).

[18] K. Nishimoto and R. Fujischiro, *Bull. Chem. Soc. Japan*, **35**, 390 (1962). Their heteroatom parameters are $h_0 = 1.5$ and $k_{CO} = 0.7$.

[19] Further investigations of the reaction products of these ion radicals are being conducted.

[20] T. Forster and K. Kasper, *Z. Electrochem.*, **59**, 977 (1955).

[21] All melting and boiling points are uncorrected.

[22] 1,7 isomer: N. P. Buu-Hoi and D. Lavit, *J. Org. Chem.*, **21**, 1257 (1956). 1,8 isomer: H. Schmid, T. M. Meijer, and A. Ebnother, *Helv. Chim. Acta.*, **33**, 595 (1950). All others are listed in Elsevier's Encyclopedia of Organic Chemistry, Series III, Elsevier Publishing Co., New York, N. Y., 1962, p 12B.

[23] Unpublished results with W. Hodgson and J. Brinen.

[24] J. Jacques, *Bull. Soc. Chim. France*, [5] **22**, 231 (1955).

procedure exactly analogous to that described for the preparation of 1-methylthionaphthalene. From 10 g (0.035 mole) of 1,4-dibromonaphthalene, 0.23 g (3%) of 1,4-bis(methylthio)naphthalene, mp 97–98° (lit.[25] 95°), was obtained after several recrystallizations from petroleum ether (bp 30–60°).

From 5.0 g (0.0175 mole) of 2,3-dibromonaphthalene, 0.15 g (4%) of 2,3-bis(methylthio)naphthalene was isolated by sublimation at 120–130° (0.1 mm), mp 82–85°. Recrystallization from methanol raised the melting point to 86–87°.

Anal. Calcd: C, 65.45; H, 5.49; S, 29.10. Found: C, 65.34; H, 5.53; S, 29.00.

1,5-Bis(methylthio)naphthalene, 2,6-Bis(methylthio)naphthalene, and 2,7-Bis(methylthio)naphthalene.—These three compounds were prepared by alkylation with dimethyl sulfate of the corresponding dithiols. The latter were prepared from the corresponding disulfonyl chlorides of naphthalene by zinc amalgam reduction. The sulfonyl chlorides were prepared from the three commercially available sodium salts of the naphthalene disulfonic acids. The salts of naphthalene 1,5-disulfonic acid and naphthalene 2,7-disulfonic acid were obtained from Distillation Products Industries while the disodium salt of 2,6-naphthalene disulfonic acid was obtained from Aldrich Chemical Co. Although the three dithiols were previously prepared,[26] 2,6-bis(methylthio)naphthalene and 2,7-bis(methylthio)naphthalene are not reported in the literature. The compounds, their melting points, over-all yields from the salt of the disulfonic acid, and analyses (for the new compounds) are as follows: 1,5-bis(methylthio)naphthalene, mp 149–154° (chloroform) (lit.[26] 150°), 18% over-all yield; 2,6-bis(methylthio)naphthalene, mp 136–138° (sublimed), 10% over-all yield.

Anal. Calcd: C, 65.45; H, 5.49; S, 29.10. Found: C, 65.42; H, 5.36; S, 28.92.

2,7-Bis(methylthio)naphthalene, mp 73–74° (ethanol), was obtained in 12% over-all yield.

Anal. Calcd: C, 65.45; H, 5.49; S, 29.10. Found: C, 65.26; H, 5.75; S, 28.82.

1,8-Bis(methylthio)naphthalene.—Treatment of 1.00 g (0.0055 mole) of 1,8-naphthalene dithiol[27] and 1.74 g (0.014 mole) of dimethyl sulfate in 150 ml of methanol with 1.98 g (0.05 mole of sodium hydroxide, dropwise at 20°, gave after refluxing on the steam bath for 1 hr and extraction with ether, 0.91 g of ether-soluble semisolid. Recrystallization from ethanol gave 0.84 g (73%) pale yellow crystals, mp 83–84° (lit.[27] 84°).

1-Dimethylaminonaphthalene and 2-Dimethylaminonaphthalene.—The former compound was obtained from Eastman Kodak Co. and was distilled before use. The latter compound, mp 45–46°, was obtained from Aceto Chemical Co.

2,6-Bis(dimethylamino)naphthalene.[28]—2,6-Diaminoanaphthalene was prepared from 2,6-dihydroxynaphthalene (Aldrich Chemical Co.), aqueous ammonia, and ammonium sulfite by a literature procedure, mp 225° (lit.[29] 217–219°).

A mixture of 4.0 g (0.025 mole) of 2,6-diaminonaphthalene, 5.6 g of calcium carbonate, 25 ml of methanol, 7 ml of water, and 13 ml of methyl iodide was refluxed for 12 hr. The resulting precipitate was filtered and crystallized from hot water yielding 8.75 g (68.5%) of crude bisquarternary salt, mp 236° dec. The crude product (8.0 g) was refluxed with a solution of sodium ethoxide in ethanol prepared from 2 g of sodium and 60 ml of ethanol for 48 hr. The mixture was cooled and the yellow precipitate was filtered, dissolved in water, and extracted with ether. The ether solution was dried with calcium chloride and filtered, and the solvent was evaporated. The residue was recrystallized twice from ethanol to yield 1.5 g (45%) of yellow needles, mp 148–150°.

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.63; H, 8.37; N, 13.52.

2,7-Bis(dimethylamino)naphthalene.[28]—A mixture of 15.8 g (0.1 mole) of 2,7-diaminonaphthalene (Koch-Light Ltd.), 22.0 g of calcium carbonate, 100 ml of methanol, 25 ml of water, and 50 ml of methyl iodide was refluxed for 10 hr. The mixture was cooled and the precipitate was filtered and recrystallized from hot water (charcoal). The white quaternary salt thus isolated (23 g) had mp 214° dec. A solution of sodium ethylate was prepared from 1.9 g of sodium and 60 ml of ethanol and to this was added 10.0 g (0.02 moles) of the above 2,7-bis(trimethylammonium)naphthalene diiodide salt. After refluxing for 30 hr, all of the solid had dissolved. Most of the ethanol was evaporated from the reaction mixture on a steam bath, and 10 ml of water was added to the residue which was then extracted with ether. The ether extracts were dried over sodium hydroxide, treated twice with charcoal, and concentrated to give an oil. Warming this oil to 40° in a sublimation apparatus at 0.5 mm resulted in a collection of 1.0 g of white needles with a strong fluorescence (15% over-all yield), mp 49–51°.

Anal. Calcd: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.20; H, 8.48; N, 12.81.

1,5-Bisdimethylaminonaphthalene.[28]—A solution containing 20.0 g (0.127 mole) of 1,5-diaminonaphthalene (Aldrich Chemical Co.) and 28.0 g of calcium carbonate in a mixture of 125 ml of methanol, 65 ml of methyl iodide, and 35 ml of water was refluxed for 8 hr. On cooling and adding water, a grey-brown precipitated, mp 75–80°, was obtained. Two recrystallizations from ethanol followed by sublimation at 85–90° (0.25 mm) gave 5.5 g (20%) of colorless, blue fluorescent crystals, mp 87–88° light brown crystals, (lit.[20] mp 90.5°).

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.52; H, 8.62; N, 13.00.

1,5-Dimethoxy-4,8-diphenoxynaphthalene.[28]—A mixture of 3.46 g (0.01 mole) of 1,5-dibromo-4,8-dimethoxynaphthalene,[4] 3.00 g (0.044 mole) of potassium phenolate, and 0.3 g of activated copper was heated in a metal bath at 230° for 90 min. The mixture was cooled and the fused mass was broken up and extracted with chloroform. The dark brown chloroform extract was passed over alumina. Evaporation of the solvent and recrystallization from chloroform gave 0.57 g of product (15.3%), mp 235–237°.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.20; H, 5.42.

1,5-Dimethoxy-4,8-bis(methylthio)naphthalene.—Cuprous methylmercaptide prepared from 100 g of methanethiol (Eastman Kodak Co.) and 44 g of cuprous chloride was prepared by a previously described method.[5] To this was added 5.6 g (0.016 mole) of 1,5-dibromo-4,8-dimethoxynaphthalene,[4] 125 ml of quinoline, and 40 ml of pyridine. The mixture was stirred and refluxed for 5 hr. The final reflux temperature was 170°. The mixture was cooled to 100° and poured into 200 ml of concentrated hydrochloric acid in 500 ml of ice and allowed to stand overnight. The product was then filtered. The filtrate was extracted with two 100-ml portions of ether and the insoluble material was pulverized and extracted with 1 l. of ether for 24 hr in a Soxhlet apparatus. The ether extracts were combined, washed with 10% HCl then water, and the dried over sodium sulfate, filtered, and concentrated to give a viscous, brown liquid. Trituration of this liquid with ether gave 0.3 g (6%) of tan solid, mp 220–240°, from which a white solid, constant mp 242–243°, was isolated after three crystallizations from heptane.

Anal. Calcd for $C_{14}H_{16}O_2S_2$: C, 59.96; H, 5.75. Found: C, 59.82; H, 5.77.

1,4,5,8-Tetramethoxynaphthalene.[28]—A mixture of 2.53 g (0.008 mole) of 1,5-dibromo-4,8-dimethoxynaphthalene, 1.08 g (0.02 mole) of sodium methoxide, and 4.29 g (0.03 mole) of cuprous oxide was refluxed in 150 ml of N,N-dimethylformamide for 20 hr. The cooled mixture was poured into excess water and the resulting precipitate was filtered and air dried. It was then dissolved in a small quantity of chloroform and passed through a small column of alumina. The fractions taken from the column were concentrated, redissolved in carbon tetrachloride, and examined by nmr. After much di- and trimethoxy-substituted material had been removed, a fraction was obtained, crude mp 154–156°, which showed a sharp, single methoxy proton peak in the nmr and a sharp, unsplit aromatic proton peak with integrated intensities nearly 3:1. Several recrystallizations from hexane gave 350 mg of white crystals, mp 167–168° (lit.[2] 170°). The nmr spectrum in carbon tetrachloride solution showed two sharp peaks at τ 6.21 and 3.28 with integrated intensities of 3:1.

1,4,5,8-Tetraphenylnaphthalene.—This compound was prepared by a literature procedure.[31]

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[25] H. S. Desai and B. D. Tilak, *J. Sci. Ind. Res. India*, **19B**, 390 (1960).

[26] J. Pollack, *Montash Chem.*, **50,** 322 (1928).

[27] W. B. Price and S. Smiles, *J. Chem. Soc.*, 2372 (1925); A. Zweig and A. K. Hoffmann, *J. Org. Chem.*, **30**, 3997 (1965).

[28] We wish to thank Miss G. Metzler for these preparations.

[29] J. Chatt and W. P. Wynne, *J. Chem. Soc.*, 33 (1943).

[30] W. G. Brown and N. J. Letang, *J. Am. Chem. Soc.*, **63**, 358 (1941).

[31] E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

9-Methoxyanthracene[28] **and 9,10-dimethoxyanthracene** were prepared from anthrone and anthroquinone, respectively, by methods described in the literature.[32]

9,10-Bis(methylthio)anthracene.—From 10.0 g (0.03 mole) of 9,10-dibromoanthracene and cuprous methylmercaptide prepared from 44.0 g of cuprous chloride and 100 of methanethiol, 0.85 g (11.6%) of lemon yellow needles, mp 161–162°, was obtained after three recrystallizations from ethanol. The procedure used was identical with that described for the preparation of 1-methylthionaphthalene.

Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.06; H, 5.22; S, 23.72. Found: C, 70.70; H, 5.31; S, 23.52.

9,10-Bis(2,6-dimethoxyphenyl)anthracene.[33]—Commercially available powdered 2,6-dimethoxyphenyllithium (20 g, lithium Corporation of America) was added all at once to 8 g of anthraquinone in 120 ml of anhydrous tetrahydrofuran. After stirring overnight at room temperature, the reaction mixture was a slurry of pale yellow solid. After pouring the formed mixture into water and acidification of the solution, a dark, bluish purple oil resulted. The aqueous mixture was thrice extracted with 100-ml portions of ether. During extraction a small amount (approximately 4 g) of colorless solid separated and was filtered. After three recrystallizations from hot pyridine, the solid had mp 342–343° dec and had an infrared spectrum and analysis consistent with its formulation as 9,10-dihydro-9,10-dihydroxybis(2,6-dimethoxyphenyl)anthracene.

Anal. Calcd for $C_{30}H_{28}O_6$: C, 74.36; H, 5.83; O, 19.81. Found: C, 74.65; H, 5.86; O, 20.05.

The diol was reduced with 3 g of zinc dust in 80 ml of glacial acetic acid after refluxing for 1 hr. After working up the solution by dilution with water followed by extraction with ether and evaporation of the solvent, 9,10-bis(2,6-dimethoxyphenyl)-anthracene was obtained as very pale yellow, small crystals. After recrystallization from pyridine it had mp 287–288° (yield approximately 2 g).

Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82; O, 14.21. Found: C, 78.83, 79.13; H, 6.28; O, 13.74, 13.97.

9,10-Bis(phenylethynyl)anthracene.[28]—This compound was prepared by a literature procedure[10] using anthraquinone and the anion of phenylacetylene.

9,10-Diphenoxyanthracene.[28]—In a round-bottomed flask, 10 g (2.03 moles) of 9,10-dibromoanthracene, 8 g (0.06 mole) of potassium phenolate, 0.1 g of activated copper, and 0.01 g of phenol was heated to 220–230° for 2 hr. The solid was cooled then powdered and extracted with chloroform in a Soxhlet apparatus. The chloroform solution was passed through a column of alumina and was then evaporated, yielding 2.65 g (22%) of material which was sublimed at 210–215° (0.2 mm) to give pale yellow crystals, mp 235–257°.

Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01; O, 8.23. Found: C, 86.48; H, 5.10; O, 8.43.

N,N′-Tetramethylbenzidine, 4-Methoxybiphenyl, and 3,3′-Dimethoxybiphenyl.—Commercially available material (Eastman Kodak Co.) recrystallized from suitable solvents were used.

4,4′-Dimethoxybiphenyl.—Commercial (Eastman Kodak Co.) *p*-biphenol (5.0 g) was methylated with dimethyl sulfate and sodium hydroxide in methanol and the product was recrystallized from benzene to give 3.4 g, mp 173° (lit.[34] 173°).

2,2′-Dimethoxybiphenyl.—This compound was prepared from 5.0 g (0.027 mole) of 2,2′-biphenol (Aldrich Chemical Co.) and dimethyl sulfate as above. After recrystallization from ethanol, 4.2 g of product, mp 154–155° (lit.[35] 155°), was obtained.

4,4′-Bis(methylthio)biphenyl.—Treatment of 31.2 g (0.1 mole) of 4,4′-dibromobiphenyl with cuprous methylmercaptide prepared from 44.0 g of cuprous chloride and 100 g of methanethiol according to the procedure described for the preparation of 1-methylthionaphthalene resulted, after recrystallization from cyclohexane then ethenol, in a 1.8-g yield of the desired product, mp 185–186° (lit.[36] 185–186°).

3,3′-Bis(methylthio)biphenyl.—*m*-Methylthioaniline (14.0 g, 0.10 mole) dissolved in 80 ml of water and 30 ml of concentrated sulfuric acid was diazotized at −5° with a solution of 7.0 g of sodium nitrite in 14 ml of water. An aqueous suspension of cuprous hydroxide was prepared by the addition of 20% sodium hydroxide to a solution of 30 g of cuprous chloride in 120 ml of concentrated hydrochloric acid until the mixture was faintly alkaline. The precipitate was washed by decantation until no alkali was present in the wash water. The diazonium salt solution was then added at 15–20° with stirring and the mixture was heated on the steam bath for 15 min. The dark, oily product was extracted with ether. The ether extracts were washed with 5% aqueous sodium hydroxide, then water, then dried over sodium sulfate and concentrated. Preparative-scale vpc was used to isolate 50 mg of the desired compound from the resulting oil, mp 54.5–55.5° (lit.[37] 50°). The nmr and infrared spectra of this compound confirmed its identity.

10,10′-Dimethoxy-9,9′-dianthrancenyl.—This compound was prepared from bianthronyl (Aldrich Chemical Co.) according to a literature procedure.[38] The product melted at 250–251° after recrystallization from acetic acid (lit.[38] 249–250°).

1,6-Bis(methylthio)pyrene.—A solution of 20.2 g (0.1 mole) of pyrene in 300 ml of carbon tetrachloride was treated with 16 g (0.1 mole) of bromine in 300 ml of carbon tetrachloride and the product was worked up in the manner described in the literature.[39] A yield of 12.5 g of 1,6-dibromopyrene, mp 218-221° (lit.[39] 223°), was thus obtained. This dibromopyrene was treated with cuprous methylmercaptide prepared from 44 g of cuprous chloride and 100 g of methanethiol in pyridine–quinoline solution and worked up in a manner as previously described to give 2.75 g of the crude desired product as a yellow powder, mp 175–185°. Repeated recrystallization from chloroform gave yellow crystals of constant melting point (196–197°).

Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79; S, 21.78. Found: C, 73.11; H, 4.57; S, 21.39.

1,6-Bis(dimethylamino)pyrene.[28]—Refluxing 232 mg (0.001 mole) of 1,6-diaminopyrene (Koch-Light Ltd.) with 220 mg of calcium carbonate, 10 ml of methanol, 2.5 ml of water, and 2.5 ml of methyl iodide for 30 hr gave a crude quanternary salt whose infrared spectrum showed NH^+ absorption. The salt was therefore treated with a fresh mixture of the same quantities of reagents and refluxed for 12 additional hr. The salt obtained showed no NH^+ absorption and had mp *ca.* 172°. This crude material was added to a solution of 1.0 g of sodium in 60 ml of ethanol and was refluxed for 2 days. The solvent was evaporated and the residue was taken up in 10 ml of water and extracted with ether. The ether layer was separated, dried, and concentrated to yield a green solid. Recrystallization from ethanol gave 350 mg (38.4%) of greenish needles, mp 163–164°; a further 300 mg of this material could be recovered by concentration of the mother liquor. Sublimation of the product at 150–160° (0.1 mm) gave yellow crystals, mp 164–165°.

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.71. Found: C, 83.02; H, 7.02; N, 9.86.

1,6-Dimethoxypyrene.[28]—To 650 g of concentrated sulfuric acid was added 150 g of anhydrous sodium sulfate. The mixture was cooled to 55° and with stirring 101 g (0.5 mole) of pyrene (Eastman Kodak Co.) was added in portions over 5 min. Stirring was continued for 15 min and then the mixture was cooled to 12° in an ice bath and 400 g of 65% oleum was added over 20 min. The mixture was allowed to warm to room temperature and was stirred overnight. The solution was poured into 2 l. of water and then saturated with sodium chloride and sodium sulfate causing the sulfonated product to precipitate (70 g). This was purified by adding just enough water to effect solution, then precipitation by addition of ethanol. Treatment of 36 g of this salt with a solution of 36 g of sodium hydroxide in 100 ml of water at 240–250° in an autoclave for 12 hr gave a precipitate which after several recrystallizations from methanol had mp 220° (2.7 g). A second run yielded 4.1 g of recrystallized diol. Alkylation of 6.6 g (0.028 mole) of this diol with 16 g (0.16 mole) of dimethyl sulfate and 7.5 g (0.13 mole) of potassium hydroxide in 125 ml of water at 20–25° gave after recrystallization from chlorobenzene a tan solid, mp 244–245° (for 1,6-dimethoxypyrene, lit. 244–246°,[40] 245°[41]).

Measurements.—The polarographic data were obtained at room temperature on a Leeds and Northrup electrochemograph Type E. Oxidations were carried out in dry (<0.01% water)

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(32) J. S. Meck, P. A. Monroe, and C. J. Bouboulis, *J. Org. Chem.*, **28**, 2575 (1963).

(33) We wish to thank A. K. Hoffmann for this compound.

(34) A. Gillmeister, *Ber.*, **30**, 2849 (1897).

(35) P. Jannasch, and E. Kolitz, *ibid.*, **31**, 1745 (1898).

(36) J. Obermeyer, *ibid.*, **20**, 2928 (1887).

(37) H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1147 (1928).

(38) E. deB. Barnett, J. W. Cook, and M. A. Matthews, *ibid.*, **123**, 1996 (1923).

(39) M. deClercq and R. H. Martin, *Bull. Soc. Chim. Belges*, **64**, 367 (1955).

(40) E. Profft and R. Biela, *J. Prakt. Chem.*, [4] **20**, 87 (1963).

(41) H. Vollmann, *et al.*, *Ann.*, **531**, 1 (1937).

acetonitrile at a rotating platinum electrode with 0.1 *M* tetra-*n*-propylammonium perchlorate as supporting electrolyte. Reductions were carried out at a dropping mercury electrode in dry ($<0.01\%$ water) N,N-dimethylformamide. An aqueous saturated calomel reference electrode was used throughout.

Preliminary fluorescence screening was done by dissolving a few milligrams of the compound in 1 ml of benzene and examining the resulting solution with a Blak-Ray UVL-22 lamp (Ultraviolet Products, Inc.)

Fluorescence spectra, ECL emission spectra, and quantum yield measuremnts were made on a combination radiometer–fluorimeter incorporating a Bausch and Lomb grating monochromator and an Aminco amplifier with a IP21 photomultiplier tube. The details of the fluorescence spectral measurements and quantum yield techniques are described elsewhere.[42] The ECL spectra were measured in a Pyrex cell containing two 80 mesh platinum gauze electrode 1 in. in diameter which were set 2 mm apart. One electrode was set against a flat glass surface of the cell whose total volume was 3.0 ml. Enough fluorescer and tetra-*n*-butylammonium perchlorate (Southwestern Analytical Co.) were added to make the resulting solution 0.005 *M* in the former and 0.1 *M* in the latter. In a nitrogen atmosphere, dry N,N-dimethylformamide was added to fill the cell which was then closed with a ₸ 14/20 stopper. The cell was placed in the combination radiometer–fluorimeter and approximately 5 v rms was placed across the electrodes with a variable transformer. The voltage setting was adjusted slightly to obtain maximum ECL emission and the spectrum was recorded. The same cell was also used to check the fluorescence spectra although reflection of the excitation light (from a G.E. F4T5/BLB fluorescent tube) by the platinum gauze caused some irregularity and this method could not be employed for accurate fluorescence spectra.

The cyclic voltammetry was carried out using an operational amplifier-based three-electrode electronic polarograph, and polarographic cells of conventional design. The ion-radical lifetimes were measured as the time it takes to go from the polarographic peak of the process in which the ion in question is formed to the peak of the reverse process at a scan rate adjusted so that the reverse peak is just detectable.

Registry No.—1-Methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; 1,3-dimethoxynaphthalene, 10075-61-3; 1,4-dimethoxynaphthalene, 10075-62-4; 1,5-dimethoxynaphthalene, 10075-63-5; 1,6-dimethoxynaphthalene, 3900-49-0; 1,7-dimethoxynaphthalene, 5309-18-2; 1,8-dimethoxynaphthalene, 10075-66-8; 2,3-dimethoxynaphthalene, 10103-06-7; 2,6-dimethoxynaphthalene, 5486-55-5; 2,7-dimethoxynaphthalene, 3469-26-9; 1,4,5,8-tetramethoxynaphthalene, 10075-68-0; 1-dimethylaminonaphthalene, 86-56-6; 1,5-bis(dimethylamino)naphthalene, 10075-69-1; 2-dimethylaminonaphthalene, 2436-85-3; 2,6-bis(dimethylamino)naphthalene, 10075-70-4; 2,7-bis(dimethylamino)naphthalene, 10075-71-5; 1-(methylthio)naphthalene, 10075-72-6; 2-(methylthio)naphthalene, 7433-79-6; 1,4-bis(methylthio)naphthalene, 10075-73-7; 1,5-bis(methylthio)naphthalene, 10075-74-8; 1,8-bis(methylthio)naphthalene, 7343-31-9; 2,3-bis(methylthio)naphthalene, 10075-76-0; 2,6-bis(methylthio)naphthalene, 10075-77-1; 2,7-bis(methylthio)-naphthalene, 10075-78-2; 1,4,5,8-tetraphenylnaphthalene, 5710-05-4; 1,5-dimethoxy-4,8-bis(methylthio)-naphthalene, 10075-80-6; 1,5-dimethoxy-4,8-diphenoxynaphthalene, 10075-81-7; 9-methoxyanthracene, 2395-96-2; 9,10-dimethoxyanthracene, 2395-97-3; 9,10-bis(methylthio)anthracene, 10075-83-9; 9,10-bis(2,6-dimethoxyphenyl)anthracene, 10075-84-0; 9,10-bis-(phenylethynyl)anthracene, 10075-85-1; 9,10-diphenoxyanthracene, 10075-86-2; 4-methoxybiphenyl, 613-37-6; 4,4′-dimethoxybiphenyl, 2132-80-1; 3,3′-dimethoxybiphenyl, 6161-50-8; 2,2′-dimethoxybiphenyl, 4877-93-4; 4,4′-bis(methylthio)biphenyl, 10075-90-8; 3,3′-bis(methylthio)biphenyl, 10075-91-9; 2,2′-bis(methylthio)biphenyl, 7343-32-0; N,N′-tetramethylbenzidine, 366-29-0; 10,10′ dimethoxy-9,9′-bianthracenyl, 10294-75-4; 1,6-bis(dimethylamino)pyrene, 10075-93-1; 1,6-dimethoxypyrene, 10103-10-3; 1,6-bis(methylthio)-pyrene, 10075-94-2; naphthalene, 91-20-3; anthracene, 120-12-7; biphenyl, 92-52-4; pyrene, 129-00-0; 9,10-dihydro-9,10-dihydroxy-9,10-bis(2,6-dimethoxyphenyl)-anthracene, 10075-95-3.

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[42] *Cf.* M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts, and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965).

Nitrocyclopentadiene

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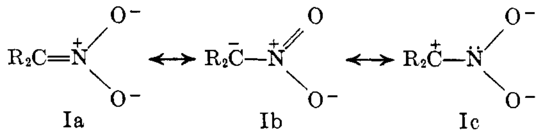
The spectral and chemical properties of the sodium salt of nitrocyclopentadiene have been investigated. Protonation occurs to give the conjugated isomer, 1-nitrocyclopentadiene, as the only simple product.

The structure of salts of nitroalkanes has been extensively studied in recent years by a variety of techniques, including ultraviolet,[1] infrared,[2] and nmr[3] spectroscopy, and, in one case, by X-ray crystallography.[4] These methods uniformly demonstrate that the structure of such salts is best represented by the formula Ia, with only small contributions from Ib and Ic. This is consistent with the chemical properties of



Ia Ib Ic

these salts, which invariably react most rapidly at oxygen with acids and other electrophiles, although thermodynamic control generally favors reaction at carbon.

An exception to the general rule that the carbon-protonated true nitro compound is more stable than

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[1] W. Kemula and W. Turnowska-Rubaszewska, *Roczniki Chem.*, **37**, 1597 (1963).

[2] (a) H. Feuer, C. Savides, and C. N. R. Rao, *Spectrochim. Acta*, **19**, 431 (1963); (b) Z. Buczkowski and T. Urbanski, *ibid.*, **18**, 1187 (1962); (c) N. Jonathan, *J. Mol. Spectry.*, **7**, 105 (1961); references therein.

[3] (a) A. A. Griswold and P. S. Starcher, *J. Org. Chem.*, **30**, 1687 (1965); (b) S. Brownstein, *ibid.*, **28**, 2919 (1963).

[4] D. J. Sutor, F. J. Llewellyn, and H. S. Maslen, *Acta Cryst.*, **7**, 145 (1954).