efficiencies shows that quenching by these agents[1] is not uniquely characteristic of chlorophyll or of chlorins, but is probably a property of all fluorescent porphyrin derivatives and perhaps also of aromatic hydrocarbons. The observed increase in efficiency of quenching for porphyrins may be due in part to the difference in solvent; benzene being used in the present experiments and methanol (or acetone) in the chlorophyll studies.

It is also suggestive that oxygen[6] and nitric oxide[7] which quench the fluorescence of chlorophyll solutions[2] are effective quenchers for solutions of a number of aromatic hydrocarbons. Nitrobenzene which is a moderately strong quencher for chlorophyll[2] has been reported[8] to quench the fluorescence of rubrene.

The quenching constants, k_1, for oxygen upon aromatic hydrocarbons, range from 180 to 2400 l./mole. The corresponding values for the porphyrins (350 and 320 l./mole) fall within this range; but, in marked contrast, the value for chlorophyll-a (in ethanol) is tenfold smaller. It is interesting to speculate whether this low quenching efficiency may be a unique property of chlorophyll, possibly related to the very low quantum yield for the autoxidation of alcoholic solutions of chlorophyll.[9]

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(6) E. J. Bowen and A. H. Williams, *Trans. Faraday Soc.*, **35**, 765 (1939).

(7) H. Weil-Malherbe and J. Weiss, *J. Chem. Soc.*, 541 (1944).

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MINNEAPOLIS, MINN. RECEIVED AUGUST 6, 1951

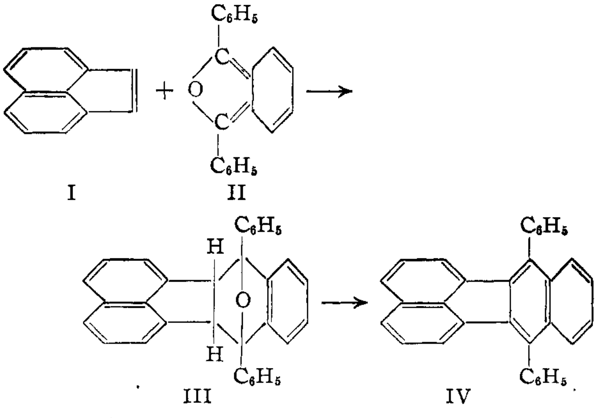
NOTES

Acenaphthylene as a Philodienic Compound

By E. BERGMANN

Four years ago,[1] the philodienic properties of acenaphthylene (I) were reported; a new synthetic route into the fluoranthene series is based on the reaction of (I) with dienes. The investigation has since been continued in this Laboratory; the results are in accord with those published some months ago by Kloetzel and Mertel.[2] Of the additional experimental material which has accumulated, the reaction between (I) and diphenylisobenzfuran (II)[3] may be reported. The normal addition product (III) which was obtained in quantitative yield when the components reacted in xylene solution, could be dehydrated to 7,12-diphenylbenz[K]fluoranthene (IV). (IV) was formed directly, when the components were heated together without solvent at 160°. This substance is the diphenyl derivative of the benz[K]fluoranthene which Orchin and Reggel[4] have obtained by cyclodehydrogenation of 1,2′-dinaphthyl and which Moureu, Chovin and Rivoal,[5] and Orchin and Reggel[6] have synthesized by unambiguous routes. Its ultraviolet spectrum is similar to that of the parent substance,[4] especially as far as the bands of longer wave length are concerned. Indeed, as in the case of 9,10-diphenylanthracene,[7] one could expect, for geometrical reasons, that the phenyl groups would not exert any bathochromic influence on the absorption spectrum.

Benz[K]fluoranthene λ (Å.)	log E_m	IV (in dioxane) λ (Å.)	log E_m
4000	4.17	4080	4.23
		3860	4.18
3710	4.13		
		3660	3.90
3595	3.90		
		3440	3.90
		3300	4.03
3095	4.83	3100	4.79
3000	4.70	2980	4.63
2850	4.43		
2695	4.37	2700	4.48
2450	4.77	2520	4.80
2175	4.60		



Adduct (III).—A mixture of acenaphthylene[2] (I) (0.6 g.) and diphenylisobenzfuran[8] (II) (1.1 g.) was refluxed in xylene (10 cc.) for 7 hours. (Part of the adduct crystallized upon cooling.) Light petroleum (50 cc.) was added, and the precipitate filtered and recrystallized from isoamyl alcohol; yellowish needles with green (in solution green-blue) fluorescence, m.p. 208°; yield, quantitative.

Anal. Calcd. for $C_{32}H_{22}O$: C, 91.0; H, 5.2. Found: C, 91.0, 91.0; H, 5.3, 5.2.

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(2) M. C. Kloetzel and H. E. Mertel, THIS JOURNAL, **72**, 4786 (1950); see also N. C. Deno, *ibid.*, **72**, 4057 (1950).

(3) For a review of the diene reactions of this compound, see ref. 1.

(4) M. Orchin and L. Reggel, THIS JOURNAL, **69**, 505 (1947).

(5) H. Moureu, P. Chovin and G. Rivoal, *Compt. rend.*, **223**, 951 (1946); **225**, 501 (1947); *Bull. soc. chim. France*, 99 (1948).

(6) M. Orchin and L. Reggel, THIS JOURNAL, **73**, 436 (1951).

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7,12-Diphenylbenz[K]fluoranthene (IV).—(a) When 1.5 g. of the adduct was refluxed for 2 hours with 10 cc. of acetic acid, containing 1 cc. of aqueous 48% hydrobromic acid, a whitish powder separated. From butyl acetate or glacial acetic acid, silvery, fluorescent leaflets were obtained. The solutions of the substance, too, show intense violet fluorescence; m.p. 267° (brown-red melt).

(b) The mixture of 2 g. of acenaphthylene and 3 g. of diphenylisobenzfuran was heated at 160° for 24 hours. The solid reaction product was triturated with butanol and recrystallized repeatedly from the same solvent; m.p. 267°; yield, quantitative.

Anal. Calcd. for $C_{32}H_{20}$: C, 95.0; H, 5.0. Found: C, 95.0; H, 5.3.

Preparation of Acenaphthylene.—Kloetzel and Mertel[8] have surveyed the known methods for the preparation of acenaphthylene. It has now been found that a most convenient method consists in the bromination of acenaphthene with NBS[9,10] and treatment of the bromoacenaphthene formed, with pyridine. It has proved advisable to work with small batches (15 g.) of the parent hydrocarbon, from which a 28% yield of acenaphthylene is obtained.

The mixture of 15.4 g. of acenaphthene, 20 g. of N-bromosuccinimide and 100 cc. of carbon tetrachloride was refluxed for 6 hours, filtered and evaporated. The residue was boiled with 80 cc. of dry pyridine for 1 hour and poured out into ice-cold dilute sulfuric acid. The precipitate was isolated by extraction with ether and purified by distillation *in vacuo;* b.p. 156–160° (28 mm.). Trituration of the distillate with ice-cold methyl alcohol gave 4 g. of acenaphthylene, m.p. 94°.

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(9) The claim of Ng. Ph. Buu-Hoi (*Ann.*, **556**, 1 (1944)) that acenaphthene is brominated by NBS in the 5-position, could not be substantiated.

(10) N-Chlorosuccinimide reacts analogously; M. F. Hebbelynok and R. H. Martin, *C. A.*, **45**, 2411 (1951).

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The Possible Use of 4f Orbitals in Bonding: the Enhanced Stability of the Higher Oxidation States of Iodine, Tellurium and Antimony; the Non-existence of Perbromic Acid

BY Z. Z. HUGUS, JR.

Compared to bromine, selenium and arsenic, elements of the second long period: iodine, tellurium and antimony show enhanced stability in their higher oxidation states and the ability to bond to greater numbers of atoms, that is to say, maximum valency. Justification for this statement is found for example in the non-existence of arsenic pentachloride, arsenic pentabromide and perbromic acid, as well as the greater oxidizing power of the oxygen acids of arsenic(V) and selenium(VI) compared to those of antimony(V) and tellurium(VI).

The present idea is that this behavior is not due to a decreased stability of the compounds of elements of the first long period, but is due to the increased stability of the analogous compounds of elements of the second long period. The factor which stabilizes the latter compounds is the contribution of 4f atomic orbitals to bonding in these compounds.

To show that the f orbitals may contribute to the bonding in iodine, tellurium and antimony compounds, it is necessary to show that in the central field approximation upon which the designation of atomic orbitals as s, p, d, etc., is based, f orbitals have the requisite symmetry to be used in bond formation in molecules of various symmetry types. By methods described by Wigner[1] and used by Kimball,[2] the irreducible representations of atomic f orbitals in a large number of symmetry point groups have been worked out. The results may be summarized here by stating that f orbitals may always be substituted for p orbitals in an hybridization complex, but only in particular symmetry groups may s and d orbitals be replaced by f orbitals. Octahedral bonding may occur with d^2sp^3 and d^2sf^3, but not f^2sp^3. According to Helmholtz[3] the IO_6^{-5} group is almost octahedral in $(NH_4)_2H_3IO_6$ and the small deviation from the regular octahedral arrangement is presumably due to hydrogen bonding forces. It thus appears that the necessity for including d orbitals in the hybridization complexes cannot be obviated by introduction of f orbitals.

In addition to possessing the proper symmetry properties, the radial portion of the f wave function must have a reasonable magnitude at the observed interatomic distances in a molecule, if f orbitals are to contribute to bonding in that molecule. The only evidence bearing on this point is the calculation of Mayer[4] using the Fermi–Thomas statistical model of the atom. She showed that the curve of the "effective potential energy" of an f electron as a function of the distance to the nucleus shows two minima, a broad outer minimum in the range 5–6 Å., and a much narrower inner minimum at about 0.2 Å., which falls very rapidly as the nuclear charge (Z) increases in the region of $Z = 57$. Evidently the outer minimum is too remote to lead to bonding at customary interatomic separations, although it might conceivably lead to rather weak long range forces in a condensed phase. In elements of Z greater than 57 the potential energy becomes positive at distances considerably smaller than the crystal radii of these elements, thus the contribution of f electrons to bonding would be expected to be nil.

In the elements preceding the rare earths the inner minimum is rather well developed. As valence electrons are removed the radius of the atom shrinks, and simultaneously the potential energy curve will fall in the region where shielding of f electrons by the valence electrons is appreciable. These effects will then coöperate to provide increasing f bonding as the degree of ionization increases. The net result is then a preferential stabilization of the higher oxidation states of the central atom.

Potential energy curves and qualitative eigenfunctions (based on the Fermi–Thomas model) indicate the possibility of a moderately large overlap integral of an f eigenfunction on iodine and a p eigenfunction on oxygen, for example.

One factor which would appear to limit the use of f orbitals in bonding is the rather large energy required to promote the valence electrons to a configuration involving f electrons. On this account one would think that rather than the hy-

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(1) E. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," Vieweg, Braunschweig, 1931.

(2) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(3) L. Helmholz, THIS JOURNAL, **59**, 2036 (1937).

(4) M. G. Mayer, *Phys. Rev.*, **60**, 184 (1941).