

of ring current on the α - and β -positions must be less than in naphthalene ($\tau \sim 0.3$). The position of the second quartet at τ 2.53 likewise indicates that the π -electron density in the 3- and 6-positions is low. The probable order of π -electron densities in I is therefore (2,7) > (1,8) > (4,5) \sim (3,6).

Now this pattern is qualitatively different from that suggested by resonance theory or simple MO theory, both of which predict high π -densities in the 2-, 4-, 5-, and 7-positions and low densities in the 1-, 3-, 6-, and 8-positions. Thus the second column of Table I shows π -densities calculated for I by the Coulson-Longuet-Higgins⁴ perturbation method, using atom-atom polarizabilities for naphthalene and with $\alpha_N = -\alpha_B = \beta$, while the third column shows results of a typical Hückel calculation (all β 's equal; $\beta = -0.7947$ e.v.; $\alpha_N = -16$ e.v.; $\alpha_B = +11$ e.v.). In each case the 1- and 8-positions are predicted to have much the lowest π -densities, and the 4- and 5-positions much the highest; on this basis the 4- and 5-protons should appear far upfield, and those in the 1- and 8-positions far downfield, from the rest. Similar results are found using any other reasonable set of parameters.

TABLE I
CALCULATED π -ELECTRON DENSITIES IN
10,9-BORAZARONAPHTHALENE

Position	Perturbational MO	Hückel MO	SCF-MO (PPP)	SCF-MO (SPO)
1	0.907	0.953	0.985	0.994
2	1.056	1.022	1.022	1.016
3	0.944	0.969	0.951	0.962
4	1.093	1.052	0.971	0.956

The last two columns of Table I list π -electron densities calculated by variants of the Pople SCF-MO method.⁵ The fourth column shows results using values for the repulsion integrals similar to those recommended by Pariser and Parr,⁶ while the last column shows results of a modified SPO calculation, with values for the integrals intermediate between the Pariser-Parr and extreme SPO values.⁷ The valence state ionization potentials of boron and nitrogen, relative to that of carbon, were taken to be -11 and $+16$ e.v., respectively. All the one-electron resonance integrals were set equal, their values being -1.7515 e.v. and -1.4907 e.v., respectively.

It will be seen that the two SCF treatments lead to predicted π -electron densities which are entirely different from those given by simple Hückel theory, and in good general agreement with experiment. Of the two sets of results, that given by the SPO method seems the better; it predicts exactly the order of π -densities that the n.m.r. spectrum seems to require.

Previous theoretical treatments of conjugated systems containing heteroatoms have been far from satisfactory. These results suggest that a semi-empirical SCF-MO treatment may prove more successful; they also emphasize the utility of aromatic boron compounds in providing a touchstone for such theories; compounds of this type can provide a crucial

(4) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).

(5) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(6) R. Pariser and R. B. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(7) Cf. A. L. H. Chung and M. J. S. Dewar, *ibid.*, in press.

test since the π -densities in them are likely to vary widely.

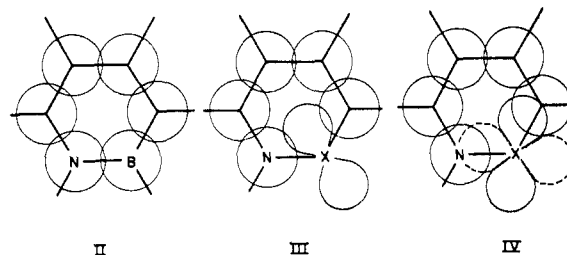
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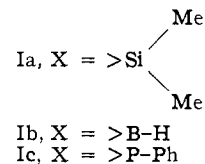
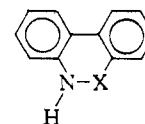
RECEIVED SEPTEMBER 18, 1964

Synthesis of a Silazarophenanthrene

Sir:



We wish to report the synthesis of 10,10-dimethyl-9,10-azasiladihydrophenanthrene (Ia) (which may also be called 10,10-dimethyl-10,9-silazarophenanthrene¹), analogous to compounds prepared by Dewar and his co-workers (Ib,² Ic³). This heteroaromatic compound,



the first of a group IV metal, was obtained by photolysis of an organosilyl azide.⁴ The successful synthetic route was discovered only after repeated attempts⁵ by more direct methods analogous to those used for heteroaromatic boron² and phosphorus³ compounds failed to give Ia. This reaction is the first example of insertion into a C-H bond by monovalent nitrogen from an organometallic azide.

The aromatic character of compounds of type I in which X is a second row element is of particular theoretical interest. Delocalization of the nitrogen lone-pair electrons into the acceptor orbital of X is expected in any case. If X is >B-H , there is only one empty orbital available, and the >N-B< (II) combination is isostructural and isoelectronic with >C=C< . If X is >P-Ph or $\text{>Si}(\text{Me})_2$, however, delocalization may occur as in III, with only one d-orbital, giving rise to phenanthrene-like molecular orbitals, or as in IV, by means of two separate d-orbitals, as is considered to be the case in $(\text{NPCl}_2)_3$.³

Whether one d-orbital or two are used for delocalization of adjacent electrons might be determined by

(1) M. J. S. Dewar in "Boron-Nitrogen Chemistry," R. F. Gould, Ed., *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1964, p. 227 ff.

(2) M. J. S. Dewar, F. Dietz, V. P. Kubba, and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961).

(3) M. J. S. Dewar and V. P. Kubba, *ibid.*, **82**, 5685 (1960).

(4) P. A. S. Smith and B. B. Brown, *ibid.*, **73**, 2435 (1951).

(5) R. E. Bailey and R. West, unpublished work.

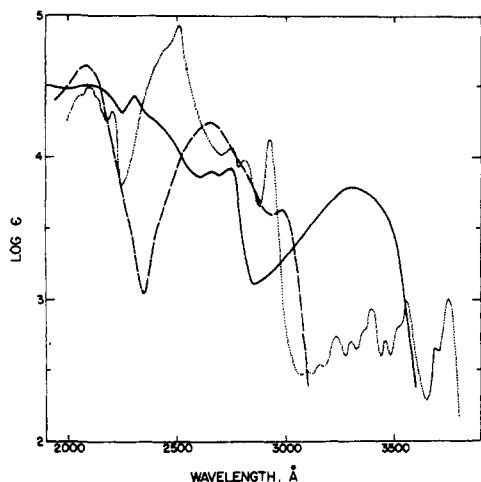


Fig. 1.—Ultraviolet spectra: —, Ia; ·····, phenanthrene; ---, 9,10-dihydrophenanthrene.

examination of ultraviolet absorption spectra, because the spectra of aromatic compounds with first-row heteroatoms substituted for carbon are similar to those of the parent hydrocarbons.^{1,6} For example, the ultraviolet spectrum of Ib is much like that of phenanthrene.⁷ The ultraviolet spectrum of Ia in isoctane shows maxima at (Å. (ε)): 3315 (6150), 2745 (8400), 2660 (7920), 2310 (26,400), 2110 (34,000), and 1930 (31,600), and is shown in Fig. 1 with the spectra of phenanthrene and 9,10-dihydrophenanthrene for comparison. The spectrum of Ia bears considerable resemblance to that of phenanthrene, suggesting that only one silicon d-orbital is used, and thus that there is aromatic character in the silicon-containing ring.

2-Lithiobiphenyl (from 2-bromobiphenyl and *n*-butyllithium), when added to excess dimethyldichlorosilane, gave $R(CH_3)_2SiCl$ ($R = 2$ -biphenyl) which was purified by distillation and refluxed with excess NaN_3 in toluene.⁸ The resulting azide, $R(CH_3)_2SiN_3$, was purified by distillation: b.p. 152° (6.5 mm.), n_D^{25} 1.5745. *Anal.* Calcd. for $C_{14}H_{13}SiN_3$: C, 66.40; H, 5.93; Si, 11.07; N, 16.60. Found: C, 66.89; H, 6.21; Si, 11.94; N, 14.86; total, 99.80. Pure $R(CH_3)_2SiN_3$ was irradiated with a low-pressure mercury arc, whereupon nitrogen gas was eliminated and ring closure took place. The solid product was separated, sublimed, and recrystallized from heptane to give Ia as large colorless cubes, m.p. 143°, in 35% yield from the azide. *Anal.* Calcd. for $C_{14}H_{13}SiN$: C, 74.60; H, 6.65; Si, 12.42; N, 6.22. Found: C, 74.11; H, 6.89; Si, 12.81; N, 6.50; total, 100.31. The infrared spectrum in benzene shows strong peaks at (cm.⁻¹) 3400 (N-H), 1460 (Si-Ph), 1330 (N-Ph), 920 (Si-N), and 1250 (Si-CH₃), together with other identifying bands.

The reactivity of Ia toward nucleophilic reagents is expected to be quite high (hydrolysis in humid air is rapid) because of the availability of four other d-orbitals, in contrast to the behavior of Ib, which has reduced reactivity because the only acceptor orbital is (partially) filled.

(6) L. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 24.

(7) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

(8) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 406 (1964).

Insertion of Si and other group IV elements into phenanthrene and other aromatic systems is under continuing investigation.^{8a}

(8a) NOTE ADDED IN PROOF.—While this work was in press, the synthesis of a heteroaromatic aluminum compound was reported by Eisch and Healy, *J. Am. Chem. Soc.*, **86**, 4221 (1964).

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Cyclo-(L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-glycyl)₂, an Active Analog of Gramicidin S

Sir:

Certain of the peptide antibiotics,¹ such as gramicidin S, cyclo-(L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-L-prolyl)₂, possess several features in common. These include a cyclic structure, D-amino acid residues, and basic character due to the presence of diamino acid residues. The efficacy of a cyclic structure for antibacterial activity is indicated by the finding that the activity of a synthetic open-chain decapeptide, with the same sequence of amino acid residues as are found in gramicidin S, is decreased markedly from that of gramicidin S.² We synthesized some 12 dipeptide anhydrides such as L-ornithyl-D-phenylalanine anhydride, because a dipeptide anhydride is the simplest cyclic peptide which has the structural features mentioned above. These compounds, however, showed no antibacterial activities.³ Furthermore, we found that a synthetic cyclic hexapeptide, cyclo-L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-L-prolyl-glycyl, showed no activity,⁴ and a decapeptide, cyclo-(glycyl-L-ornithyl-L-leucyl-D-phenylalanyl-glycyl)₂, showed very weak activity.⁵ It has also been reported that certain cyclic decapeptides such as homogramicidin S exhibited antibacterial activities.⁶

We wish to report the synthesis of a highly active analog of a gramicidin S in which a glycine residue has replaced the proline residue. This analog, cyclo-(L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-glycyl)₂, has been synthesized as follows. Carbobenzoxy-D-phenylalanyl-glycine ethyl ester (I),⁷ m.p. 109–110°, $[\alpha]_D^{25} +19.5^\circ$ (*c* 2, methanol), was prepared by coupling carbobenzoxy-D-phenylalanine with glycine ethyl ester by the dicyclohexylcarbodiimide procedure. I was converted to oily D-phenylalanyl-glycine ethyl ester hydrochloride (II) by catalytic hydrogenation in a yield of 97%. Reaction of carbobenzoxy-L-leucine with II by the dicyclohexylcarbodiimide method gave carbobenzoxy-L-leucyl-D-phenylalanyl-glycine ethyl ester, yield 66%, m.p. 113–115°, $[\alpha]_D^{25} +13^\circ$ (*c* 2, methanol) (*Anal.* Calcd. for $C_{27}H_{35}O_6N_3$: C, 65.17;

(1) R. O. Studer and K. Vogler, *Helv. Chim. Acta*, **45**, 394 (1962).

(2) B. F. Erlanger and L. Goode, *Nature*, **174**, 80 (1954); *Science*, **131**, 669 (1960).

(3) N. Izumiya and M. Winitz, presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960; N. Izumiya, T. Kato, Y. Fujita, M. Ohno, and M. Kondo, *Bull. Chem. Soc. Japan*, in press.

(4) T. Kato, M. Kondo, M. Ohno, and N. Izumiya, *ibid.*, in press.

(5) T. Kato, M. Ohno, M. Kondo, Y. Fujita, and N. Izumiya, 6th International Congress of Biochemistry, New York, N. Y., 1964 p. 159.

(6) (a) R. Schwyzler and P. Sieber, *Helv. Chim. Acta*, **41**, 1582 (1958); (b) German Patent; *Chem. Abstr.*, **57**, 949 (1962).

(7) O. K. Behrens, D. G. Doherty, and M. Bergmann, *J. Biol. Chem.*, **136**, 61 (1940).