the ester bond than the collapse of a metastable intermediate. More important is the observation that acetate and formate ions act as general-base catalysts and acetic acid and formic acid act as inhibitors of the neutral water rate. Thus in (3) acetic acid and formic acid can replace hydronium ion as general-acid catalysts and acetate and formate ions can replace water as general-base catalysts. Only a steady-state assumption allows the derivation of an equation consistent with the experimental data obtained in acetate and formate buffers. The value of $k_{\rm H_2O}/k_{\rm D_2O}$ at $a_{\rm H} = a_{\rm D}$ for acetate was determined to be 2.1. From (2) and (4) $k_1 = 0.433$ min.⁻¹ and k_2/k_3 , the partitioning coefficient, = 2.86. As would be predicted from (3), k_2/k_3 increased in deuterium oxide solution to 4.95.

The reaction of ethyl trifluorothiolacetate with other oxygen nucleophiles as well as with nitrogen nucleophiles has been investigated and will be reported in detail. Whereas in the hydroxylaminolysis and methoxylaminolysis of thiol esters and lactones the partitioning is symmetrical, in both general-base and general-acid catalysis, the reaction discussed herein must involve unsymmetrical partitioning. On the basis of this study it is clear that the requirement of microscopic reversibility should not be confused with any requirement for symmetry.

Acknowledgments.—This study was supported by grants from the National Institutes of Health and the National Science Foundation.

(4) Postdoctoral fellow of the Department of Biological Sciences, University of California, Santa Barbara.

(5) To whom inquiries should be addressed.

Departments of Biological Sciences and Chemistry Leo R. Fedor⁴ University of California, Santa Barbara Santa Barbara, California Thomas C. Bruice⁵ Received November 11, 1964

Synthesis and Nuclear Magnetic Resonance Spectrum of 10,9-Borazaronaphthalene¹

Sir:

During the past six years a new series of heteroaromatic compounds has been reported in which boron atoms appear in six-membered aromatic rings.² We have now prepared one of the more interesting members of this series, 10,9-borazaronaphthalene (I), a compound isoelectronic with naphthalene but containing no boron-free aromatic rings.



Treatment of 1-chloro-3-butene (200 g.) with liquid ammonia (350 g.) in an autoclave at 100° gave a mixture of the known 3-butenylamine (61 g.) together with

di-3-butenylamine (II) (38 g.), b.p. 153-155°.3 Hydroboration of II (25 g.) with trimethylamine borane (15 g.) in boiling toluene gave octahydro-10,9-borazaronaphthalene (III, 2.8 g.), b.p. 73-75° (20 mm.), as a colorless oil which oxidized rapidly in air. Anal. Found: C, 68.6; H, 12.1; N, 10.8. The structure of III was confirmed by its mass spectrum and by its n.m.r. spectrum which showed peaks at τ 7.1, 8.5, and 9.1 in the ratio 1:2:1; the peak at low field corresponds to a methylene adjacent to nitrogen and that at high field to one adjacent to boron. Dehydrogenation of III (3.6 g) over palladized charcoal at 300-350° gave, after chromatography on alumina, I (0.1 g.), which after sublimation formed colorless plates, m.p. 41-43°. Anal. Found: C, 74.5; H, 6.3; N, 10.6. The high-resolution mass spectrum showed peaks at 128.0782 \pm 0.0004 and 129.0743 \pm 0.0006 mµ. (Calcd. for C₈H₈NB¹⁰: 128.0786. Calcd. for C₈H₈NB¹¹: 129.0750.)

10,9-Borazaronaphthalene forms colorless plates, resembling naphthalene in both appearance and odor. Its chemical and physical properties are consistent with its formulation as a new aromatic system, isomeric with 2,1-borazaronaphthalene,² and the proton n.m.r. spectrum is also consistent with this. It consists of a well-defined doublet centered at τ 2.28, a welldefined quartet at τ 3.36, and lines in the region τ 2.5-2.8 that can be interpreted as a doublet centered at 2.67 and a quartet at 2.53. Evidently a ring current must be present since at least one pair of β protons shows a resonance in the "aromatic" region, and any inductive effects of nitrogen or boron would be small in the β -positions.

The low-field doublet must clearly be assigned to the 1- and 8-protons, adjacent to nitrogen; likewise the high-field quartet must be ascribed to the 2- and 7protons rather than the 3- and 6-protons, since all theories agree in predicting a much higher π -electron density at the 2- and 7-positions of I than at the 3and 6-positions and since no other effect could account for the large difference between the two pairs of β protons. The doublet at τ 2.67 must then be assigned to the 4- and 5-protons and the quartet at τ 2.53 to the 3- and 6-protons. The spacings of the multiplets are consistent with this assignment, the coupling constants for pairs of vicinal protons being $J_{12} = 6.5$, $J_{23} = 6.0$, and $J_{34} = 10.0$ c.p.s. Fine structure in the quartet at τ 3.36 indicates that there are also small long-range couplings.

If these assignments are accepted, some unexpected conclusions follow concerning the π -electron distribution in I. Data for other compounds (e.g., III) indicate that signals for protons α to boron are shifted upfield relative to those α to nitrogen by ca. τ 2, due to the inductive effects of nitrogen and boron; in I the difference (τ 0.39) between the 1- and 8-protons and the 4- and 5-protons is very much less than this. It seems clear that the π -electron density at the 1- and 8-positions of I must be much greater than at the 4and 5-positions. The position of the quartet at τ 3.36 likewise indicates that the π -electron density must be much greater in the 2- and 7-positions than elsewhere, for inductive effects of nitrogen and boron must be small in the β -positions of I, while differential effects

⁽¹⁾ This work was supported by grants from the Robert A. Welch Foundation and the National Institutes of Health, U. S. Public Health Service (Grant No. CA 07172-01).

⁽²⁾ See 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.

⁽³⁾ All new substances gave satisfactory analyses.

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 atomatom polarizabilities for naphthalene and with $\alpha_N =$ $-\alpha_{\rm B} = \beta$, while the third column shows results of a typical Hückel calculation (all β 's equal; $\beta = -0.7947$ e.v.; $\alpha_{\rm N} = -16$ e.v.; $\alpha_{\rm B} = +11$ 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-BORAZARONARHTHAL

10,9-DORAZARONAPATRALENE				
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 semiempirical 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

(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.

DEPARTMENT OF CHEMISTRY MICHAEL J. S. DEWAR THE UNIVERSITY OF TEXAS GERALD JAY GLEICHER Austin, Texas 78712 BRIAN P. ROBINSON

RECEIVED SEPTEMBER 18, 1964

Synthesis of a Silazarophenanthrene



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 $>Si(Me)_2$, 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 $(NPCl_2)_{3.3}$

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

⁽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)

⁽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.