12672) and the National Science Foundation for an undergraduate research fellowship (to H. R. P.).

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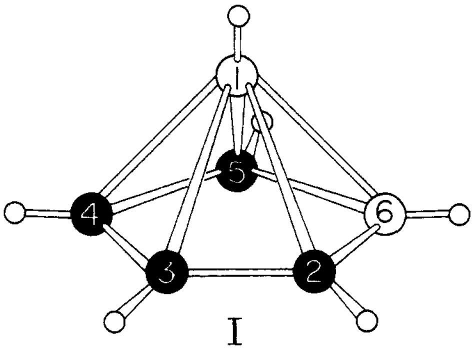
Preparation of the Pentagonal Pyramidal Carborane, 2,3,4,5-Tetracarba-*nido*-hexaborane(6)

Sir:

We wish to report the synthesis of 2,3,4,5-tetracarba-*nido*-hexaborane(6), I (Figure 1), from 1,2-tetramethyldiborane(6). The conversion was accomplished at 550° using a high-vacuum system which permits a rapid flow of gaseous reactant[1,2] through the hot zone at low pressures. In addition to the carborane, $C_4B_2H_6$, in low yield, a number of other carboranes are also produced. The experimental details of this reaction and the nature of the side products will appear in a longer dissertation at a later date.



I

Figure 1. Ball and stick model of $C_4B_2H_6$.

The evidence used to establish the formula and structure of this parent four-carbon two-boron carborane is outlined.

(a) The mass spectrum of the product purified by repeated vacuum fractional distillation exhibits a sharp cutoff at *m*/*e* 76 (calcd for $^{12}C_4{}^{11}B_2H_6$). When the parent envelope of peaks of the polyisotopic spectrum is subjected to a monoisotopic boron analysis a good fit is found for a compound consisting of two boron atoms.

(b) The ^{11}B nmr at 32.1 MHz exhibits two sharp doublets in an area ratio of 1:1 with chemical shifts (parts per million relative to boron trifluoride ethyl etherate) and coupling constants of +60.8 ppm (202 Hz) and −10.4 ppm (144 Hz). This is consistent with two B–H groups, with the high-field doublet assigned to one of these groups in an apical environment of a pyramid and the low-field doublet assigned to a basal position.[3]

(c) The proton nmr taken at both 100 and 220 MHz consist of two slightly broadened singlet resonances at (relative to τ 10.00 ppm for TMS) τ 5.38 and 4.24 ppm of equal area which are assigned to the two different kinds of carbon-attached hydrogens of I, and also two equal-area 1:1:1:1 quartets at 6.08 (J = 141 Hz) and 10.59 ppm (J = 205 Hz) which are assigned to H–^{11}B(6) and H–^{11}B(1), respectively.[4] The area of each quartet is almost one-half of the area of each H–C singlet. The chemical shifts of all of the protons are reasonably within the range of values found for other pyramidal systems containing a different number of carbon and boron atoms in the series $C_nB_{6-n}H_{10-n}$ (*i.e.*, n = 0–3).[3]

(d) The most informative portions of the infrared spectrum are consistent with the assigned structure, *i.e.*, bands at 2950 (C–H) and 2570 cm^{-1} (B–H) and an absence of peaks in the B–H–B bridge regions.

In the pentagonal-pyramidal series of isoelectronic compounds $C_nB_{6-n}H_{10-n}$, the parent and/or monomethyl derivatives of those with n = 0, 1, 2, or 3 have been previously prepared and reasonably well structurally characterized. The present work adds to the parent compounds in the series a compound in which n = 4. It should be pointed out, however, that the permethyl[5] and perphenyl[6] derivatives of $C_4B_2H_6$ have been previously reported and the structures tentatively, but inconclusively, assigned. The data we present, however, leave little doubt about the identification and structural characterization of the parent $C_4B_2H_6$.

Acknowledgment. This project was supported, in part, by the Office of Naval Research. The Varian HA-100 nmr spectrometer was obtained through Grant No. GP-8347 from the National Science Foundation and the HR-220 at the California Institute of Technology was available through NSF Grant No. GP-8540.

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(2) H. H. Lindner and T. Onak, *ibid.*, **88**, 1886 (1966).

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(4) Smaller septets within each quartet are partially visible and are attributed to H–^{10}B contributions.

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(6) F. Joy, M. F. Lappert, and B. Prokai, *J. Organometal. Chem.*, **5**, 506 (1966); M. F. Lappert, "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, p 455.

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Solubilization of Alkali Metals in Tetrahydrofuran and Diethyl Ether by Use of a Cyclic Polyether

Sir:

We wish to report a new technique for dissolving alkali metals in solvents in which they are ordinarily either insoluble or only slightly soluble. This method may extend the range of solvents in which the properties of relatively stable solutions of solvated electrons and other species common to metal–amine solutions[1,2] can be studied. Of particular interest would be the ability to make extended comparisons with the properties of solvated electrons produced by pulse radiolysis.

The basis for this increased solubility is the ability of certain cyclic polyethers to complex alkali metal cations.[3,4] Noting that stabilization of the cations

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(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

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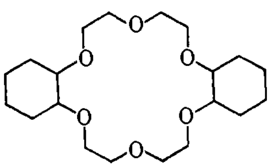
should increase the solubility of the metals, we studied the effect of adding cyclohexyl-18-crown-6,[5] **1**, to tetrahydrofuran (THF) and diethyl ether (Et_2O) in the presence of a mirror of potassium. With both solvents,



1

deep blue solutions were formed. Solutions of both potassium and cesium in THF formed readily at room temperatures and were stable for several hours even in the absence of excess metal. Metal concentrations of about 1×10^{-4} *M* were obtained by using 5×10^{-3} *M* solutions of **1**. Solutions stored at −78° for several days showed no visible signs of decomposition. In order to form solutions of potassium in Et_2O it was necessary to first cool the system to −78°. Once formed, however, the blue solutions in this solvent were stable at room temperatures for 5–10 min and for hours at −78°. At this writing only the three metal–solvent pairs described above have been examined. It is probable that many other systems will behave in a similar fashion.

It has been reported[6] that very dilute solutions of potassium in THF exhibit two epr signals, a four-line pattern characteristic of the potassium monomer and a single narrow line attributed to the solvated electron. In the presence of **1**, however, the much more concentrated potassium solutions in THF used in this work showed only a single epr line. In Et_2O at 25°, in addition to the single line ($C \simeq 10^{-7}$ *M*) a weak four-line pattern ($C \simeq 10^{-8}$ *M*, $A \simeq 11$ G) was observed, probably attributable to the potassium monomer. Both absorptions in Et_2O were absent at 0° and appeared upon warming to room temperature. The single line observed in THF solutions could be observed down to the freezing point of the solvent. In both solvents at low temperatures (−60° and below) a weak seven-line pattern was observed. The splitting value and relative intensities indicate that this absorption is probably from the benzenide anion.[7] This identification was strengthened by adding small amounts of benzene to a similar solution of potassium in THF containing **1**. The result was a marked increase in the intensity of the epr pattern but no change in the number of lines or the splitting value.

The epr results indicate that the relative concentration of monomer decreased when **1** is present. They also show, in comparison with the optical spectra, that only a small fraction of the total dissolved metal gives an epr pattern, a result which is consistent with the behavior of metal–amine solutions.[8]

The optical absorption spectra measured at room temperatures with a Beckman DK2 spectrophotometer are shown in Figure 1. These spectra have been corrected for decomposition by interpolating the results from successive scans. Potassium in THF in the presence of an excess of **1** showed only a single band with a maximum at 11,100 cm^{-1}, while the band maximum for cesium solutions occurred at 9700 cm^{-1}. With Et_2O the band maximum for potassium occurred at 11,400 cm^{-1} and a shoulder (probably caused by sodium from the Pyrex container[9]) was observed at ~14,000 cm^{-1}. These peaks can be identified with the corresponding metal-dependent "R-bands" in metal–amine solutions.[1,2] Even when the absorbance at the peak was ~3 in Et_2O (as judged by the positions of unit absorbance, 9500 and 16,000 cm^{-1}) there was no detectable absorption in the region from 8000 to 4000 cm^{-1}. A similar search was not possible for solutions in THF because of the strong solvent absorptions in this region. The absence of an optical band for the solvated electron is not necessarily at variance with the presence of an epr signal attributed to this species. The estimated spin concentration of 10^{-7} *M* is an order of magnitude below that which would have been detected optically.

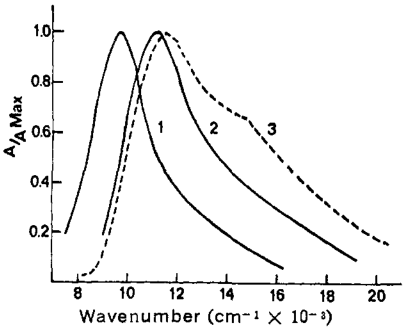


Figure 1. Absorption spectra in the presence of **1**: (1) cesium in THF, (2) potassium in THF, (3) potassium in Et_2O.

Similar absorption bands in metal–amine solutions have been attributed to the alkali anion, M^-.[10] The absence of hyperfine splitting by the potassium nucleus in THF in the presence of **1** contrasts with the results in THF alone[6] and indicates that the equilibrium

$$M \rightleftarrows M^+ + e^- \tag{1}$$

is shifted to the right by the complexation equilibrium

$$M^+ + \mathbf{1} \rightleftarrows \text{complex} \tag{2}$$

Presumably the solubility equilibrium

$$2M(s) \rightleftarrows M^+ + M^- \tag{3}$$

is similarly shifted to the right. However, the absence of a solvated electron absorption band and the very low concentration of unpaired spin indicate that the equilibrium

$$M^- + \mathbf{1} \rightleftarrows \text{complex} + 2e^- \tag{4}$$

lies far to the left in these solvents.

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(5) See ref 3 for a discussion of the nomenclature of this class of compounds.

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Nemours Co. for providing us with a sample of the crown compound.

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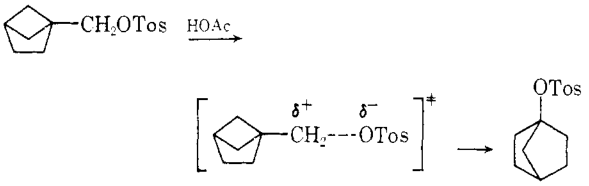
Received June 12, 1970

Vertical Stabilization of Cations by Delocalization of Strained σ Bonds[1-3]

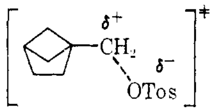
Sir:

We wish to report a successful demonstration that strained σ bonds can supply electrons by delocalization and that this delocalization is a "vertical"[3a,g] σ–π conjugation in the systems studied.

Of the various concepts which might be applicable to the solvolysis of alkyl systems, as illustrated below for 1-[2.1.1]bicyclohexylmethyl tosylate (eq 1),

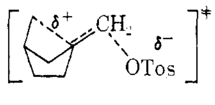


(1)



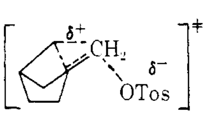
classical ionization[5]

I



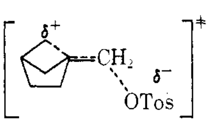
fragmentation[6]

II



bridging[4]

III

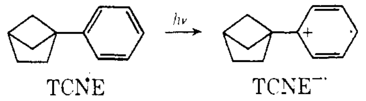


vertical delocalization[3g]

IV

two kinds of differentiation are evident. First, I postulates no σ-bond delocalization and thus differs from II, III, and IV. Second, IV differs from II and III because both II and III require nuclear movement in the strained system and can therefore be classified as "nonvertical stabilizations."[3a,g]

The recent development of quantitative correlations between solvolysis rates and ionization potentials[3g] makes possible both kinds of differentiations and allows us to decide which of the four concepts most accurately describes transition states for RCH_2X solvolyses. We here compare the relative rates of solvolysis of RCH_2X (*e.g.*, reaction 1) with the charge-transfer frequencies of the RC_6H_5–tetracyanoethylene (TCNE) complex (*e.g.*, reaction 2). In both cases some positive charge is created α to a strained bond. However, the process



(2)

(eq 2) is vertical. If the classical mechanism (1) were applicable and the solvolysis (eq 1) were faster than solvolysis of neopentyl tosylate because of steric effects, then the charge-transfer frequency should increase with increasing strain in R of RC_6H_5 because the increasing s character in the R–C bond causes inductive electron withdrawal.[7,8] If mechanism IV were important then the frequency should decrease with increasing strain.[3g,9] However the contribution to rate acceleration from bond stretching (fragmentation) or bond making (bridging) would not be detected in the vertical process (eq 2). For this reason, a good correlation between reactions 1 and 2 is an implication[10a] that neither II nor III is very important in reaction 1.[10b]

We list the charge-transfer frequencies of a series of RC_6H_5 along with relative rates of solvolysis of RCH_2X in Table I and plot the data in Figure 1.

Considering that Figure 1 plots the solvolysis rates for alkyl derivatives (RCH_2X) against essentially the aromatic σ^+ substituent constants[3g] and that the relative rates span about 10^8, the correlation is remarkably good.[13] This correlation implies that acceleration of the reaction (eq 1) is primarily due to a vertical electronic effect involving σ–π conjugation of one or more of the strained bonds. Strained or polarized[3] σ bonds

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[1] Supported by the Air Force Office of Scientific Research, Grant No. AFOSR-69-1639. Some of the precursors used were synthesized for other purposes under Army Office of Ordnance Research, Durham, Grant No. DAHC-44-69-3-0060.

[2] Some of this work was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract No. P 39.

[3] (a) The term "vertical stabilization" is defined as that stabilization which the group R supplies to a cation, $R\text{-}C^+R_2'$, or radical, $R\dot{C}R_2'$ (or the corresponding transition states), without any nuclear movement within the group R. This effect is discussed in more detail in ref 3g. Previous papers dealing with this subject are the following: (b) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965); (c) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967); (d) T. T. Tidwell and T. G. Traylor, *ibid.*, **88**, 3442 (1966); (e) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967); (f) J. A. Mangravite and T. G. Traylor, *ibid.*, 4457 (1967); (g) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

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[5] (a) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); (b) H. C. Brown, *Chem. Soc., Spec. Publ.*, **16**, 140 (1962).

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[9] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969), observed that strained hydrocarbons have lower ionization potentials than their unstrained isomers and it follows that strained σ bonds are therefore more delocalizable than unstrained σ bonds.

[10] (a) But as a referee has pointed out, certainly not a proof, because our correlation could result from a proportionality between a nonvertical stabilization in solvolyses and a vertical charge-transfer stabilization. However the size of the vertical stabilization by strained bonds makes it quite clear that a large fraction of total acceleration in these solvolyses is available without nuclear movement. (b) This implication is made stronger if it is assumed that the cyclopropyl group provides vertical stabilization. References 11 and 12 summarize a plethora of evidence that this is probably true.

[11] (a) R. C. Hahn, T. F. Corbin, and H. Shechter, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p 35-O; (b) R. C. Hahn, T. F. Corbin, and H. Shechter, *J. Amer. Chem. Soc.*, 90, 3404 (1968).

[12] E. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 111.

[13] This correlation also suggests a simple means of predicting relative solvolysis rates. For instance, we believe that we can guess the rate of solvolysis of RR′CHX fairly accurately from the color of the TCNE complex with $RR'C{=}C(CH_3)_2$. This prediction will, of course, fail where nonvertical acceleration is important. Notice the very large rate predicted for homocubylcarbinyl derivatives.