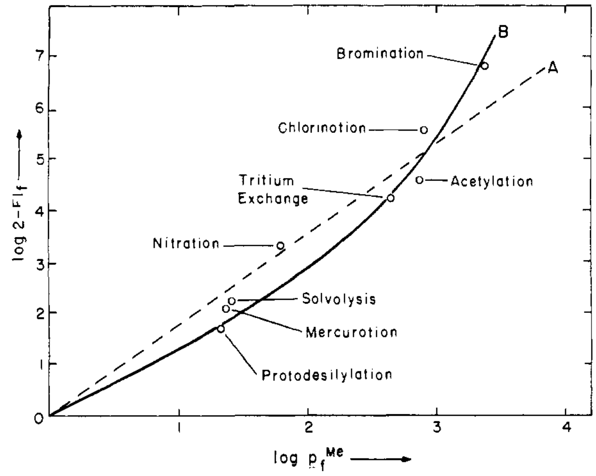

Fig. 1.—Log 2 − Fl_f vs. log p_f^{Me} for S_E reactions.

In Fig. 1, line A is the best least-squares straight line through the available points which passes through the origin.[2] The standard deviation of points from this line is 0.6. It can be seen that the arbitrary curve B fits enough better to suggest that the data, although scattered, may contain a trend similar to that shown by data for biphenyl. If biphenyl and fluorene really differ with regard to the Selectivity Relationship, a plot of log 2 − Fl_f vs. log p_f^{Ph} should show a marked curvature. However, (see Fig. 2) the best least-squares line with zero intercept[2b] shows that the data fit a more reasonable linear relationship than line A, Fig. 1. The standard deviation of points from the line is 0.4. Two points for nitration in acetic anhydride are shown in Fig. 2. The point farthest from the line corresponds to a value p_f^{Ph} = 11, obtained by Dewar.[3] The point closer to the line is obtained from an average of the values, p_f^{Ph} = 32.6 and 38.0, obtained by Simamura[4] and Norman.[5] The least-squares line in Fig. 2 was obtained from an average of these two points.[6]

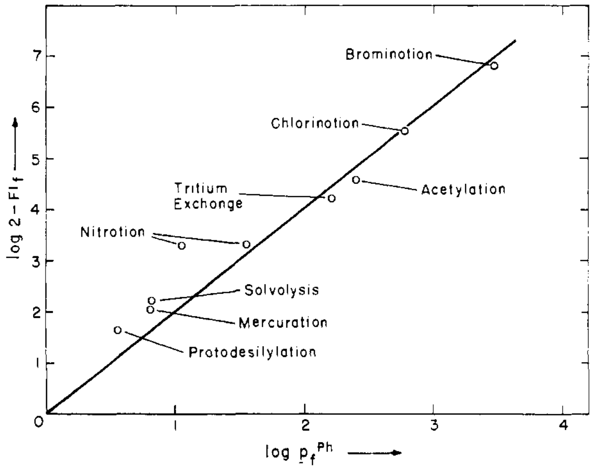

Fig. 2.—Log 2 − Fl_f vs. log p_f^{Ph} for S_E reactions.

On the basis of the available data we are led to the conclusion that $\sigma^+_{2-\mathrm{Fl}}$ is at least as good, and probably a better linear function of $\sigma^+_{p-\mathrm{Ph}}$ as of $\sigma^+_{p-\mathrm{Me}}$, and that apparently fluorene does not fit the Selectivity Relationship much better than biphenyl.

It is reasonable to attribute the much lower reactivity of biphenyl as opposed to fluorene to the deviation from planarity in the biphenyl system. However, since biphenyl and fluorene (on the basis of available data) both show greater participation of the phenyl substituent as the electron demand of the attacking reagent becomes larger, it is unreasonable to say that biphenyl is a special case due to its nonplanar geometry. *A priori* the 0.4 kcal.[1] barrier to rotation in biphenyl should be no more special than ionization potentials of other types of substituents which are of the order of 7–11 electron volts. In every case, maximum stabilization of transition states depends upon an energy balance. Thus, in general, it would be expected that the different electron demand of various electrophiles would solicit a correspondingly variable response by the substituent group. This idea has been discussed by a number of workers and has most recently been demonstrated and discussed by Knowles, Norman and Radda.[8]

Acknowledgment.—The author wishes to acknowledge the helpful assistance and counsel of Professor George S. Hammond.

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[2] (a) The form of the relationship used in Fig. 1 is log 2 − Fl_f = ($\sigma^+_{2-Fl}/\sigma^+_{p-\mathrm{Me}}$) log p_f^{Me}.[1] 2 − Fl_f is the partial rate factor for substitution in one of the 2-positions of fluorene and p_f^{Me} is the partial rate factor for substitution in the para position of toluene. (b) The requirement that the line pass through the origin is discussed by Brown [*J. Am. Chem. Soc.*, **77**, 2300 (1955)].

[3] F. B. Deans, C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 3031 (1959); P. B. D. de La Mare and M. Hassan, *ibid.*, 3004 (1957); M. J. S. Dewar, T. Mole and E. W. T. Warford, *ibid.*, 3576 (1956).

[4] O. Simamura and Y. Mizuno, *Bull. Chem. Soc., Japan*, **30**, 196 (1957).

[5] C. J. Billing and R. O. C. Norman, *J. Chem. Soc.*, 3885 (1961).

[6] Nitration data for fluorene[7] are referred to benzene through Dewar's nitration data[3] for biphenyl, which disagree with those of Simamura[4] and Norman.[5]

[7] M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 3079 (1958).

[8] J. R. Knowles, R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

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RECEIVED MAY 19, 1962

ISOMERS OF $B_{20}H_{18}^{-2}$

Sir:

There are to date no known isomers among molecular or ionic species containing only boron and hydrogen, presumably owing to facile rearrangement of both B and H geometries in electron deficient situations. We wish to report an isomer of $B_{20}H_{18}^{-2}$ ion as the first example.

It has been reported[1] recently that Fe^{+3} oxidation of the $B_{10}H_{10}^{-2}$ ion, the proposed[2] structure of which has now been proven,[1] produces centrosymmetric[3] $B_{20}H_{18}^{-2}$ (ion A; m. p. of $HNEt_3^+$ salt, 173–174°). The B^{11} nuclear magnetic resonance

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[1] A. Kaczmarczyk, R. D. Dobrott and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **48**, 729 (1962).

[2] W. N. Lipscomb, A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

[3] B. Dickens and W. N. Lipscomb, X-ray diffraction study in progress.

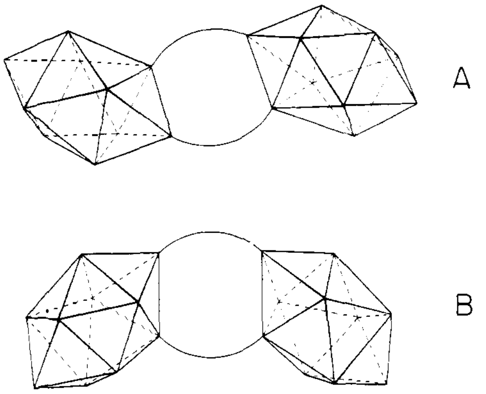

Fig. 1.—Proposed structures for $B_{20}H_{18}^{-2}$ ions A and B. The low field singlet and doublet in the B^{11} n.m.r. spectra of ions A and B are essentially identical, but the high field regions are different enough to indicate different structures for A and B, but not different enough to indicate that the B_{10} units have been destroyed in the preparations for A and B. Each curved line is a bridge hydrogen. Terminal hydrogens are not shown.

(n.m.r.) spectrum[1] of ion A is similar enough to that of $B_{10}H_{10}^{-2}$ to suggest that the polyhedron is retained, and is strongly suggestive of modification of one apex BH bond and at least one equatorial BH bond of each original $B_{10}H_{10}^{-2}$. The proposed structure (Figure 1) is the only one consistent with the present form of the valence theory.[4]

We now wish to report that oxidation of the triethylammonium salt of $B_{10}H_{10}^{-2}$ with two equivalents of cold acidified aqueous Ce^{+4} ion precipitates the triethylammonium salt of another $B_{20}H_{18}^{-2}$ ion, B. Ion B has been converted quantitatively into ion A in aqueous solutions containing a catalytic amount of HCl, and we therefore suspect that Ce^{+4} attack at a more negative apical region of $B_{10}H_{10}^{-2}$ leads mechanistically to ion B. Probably also, isolation of A from the Fe^{+3} oxidation results from the acid catalyzed conversion of B to A at higher temperatures at which the $HNEt_3^+$ salt of B is more soluble. At higher temperatures ion A is formed exclusively in these oxidations.

The idea that the B_{10} units are preserved in ions A and B is supported (a) by infrared spectra which have a 1890 cm.$^{-1}$ band in B and a 2500 cm.$^{-1}$ band in A suggestive of symmetrical and unsymmetrical H bridges, respectively, and (b) by the B^{11} n.m.r. spectra which are strongly indicative in both ions of modification of one apex and at least one equatorial BH group of each B_{10} unit. Hence, the proposed structure of isomer B involves one apex–apex H bridge and one equatorial–equatorial H bridge. The acid catalyzed isomerization of B to A is presumed to occur by an unusual process[1] in which the bridges are not broken, but in which changes from 4 to 5 and from 5 to 4 coördination occur by slight movement (0.5 Å. or less) of the appropriate B atoms.[1] Further studies of these structures and of the isomerization mechanism have been initiated.

This new triethylammonium salt of $B_{20}H_{18}^{-2}$ (B) melts at 203–204°, shows ion aggregation in various somewhat polar solvents, and has an X-ray diffraction pattern unlike that of the corresponding salt of ion A. *Anal.* for this salt of ion B: Calcd. for $C_{12}H_{50}B_{20}N_2$: C, 32.85; H, 11.40; N, 6.39; B, 49.36. Found: C, 32.70; H, 11.80; N, 6.35; B, 49.20. Visible and ultraviolet absorbtion maxima are at 292 mμ (ϵ = 10,800) and 232 mμ (ϵ = 23,800) for ion A, at 292 mμ (ϵ = 4,880) and < 200 mμ for ion B, and < 210 mμ for $B_{10}H_{10}^{-2}$, all taken in acetonitrile solutions. The similarity of the 292 mμ band in A and B is striking, and is apparently associated with polyhedron–polyhedron interaction, since it is not present in the $B_{10}H_{10}^{-2}$ spectrum.

This research was supported by Army Ordnance Contract DA-O18021-ORD-11878 with the Rohm and Haas Company, and by the Office of Naval Research.

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RECEIVED MAY 23, 1962

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[4] W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1791 (1961).

THE RELATIVE IMPORTANCE OF C–H BOND ENERGY AND ALKYL INTERFERENCE IN RECOIL TRITIUM REACTIONS WITH ALKANES[1]

Sir:

The radioactive products have been analyzed for the reactions of recoil tritium atoms with many individual hydrocarbons, and have been shown to be formed predominantly by reactions occurring at above-thermal energies.[2–6] The detailed course of such atomic reactions in the low electron-volt region is not very well known, and further information concerning the mechanism and energetics of these processes is very desirable. Since approximately 90% of all of the recoil tritium atoms which react with alkanes while "hot" lead to HT or the labeled parent molecule[2] by (1) or (2), these two reactions are of central importance in the understanding of the chemistry of such energetic species.

$$T^* + RH \longrightarrow HT + R\cdot \qquad (1)$$

$$T^* + RH \longrightarrow RT + H\cdot \qquad (2)$$

The relative yields of HT and labeled parent have previously been measured for ten alkanes with yield ratios (HT/RT) between 1.0 and 3.6. These ratios have been shown to correlate satisfactorily with the formula

$$\frac{HT}{RT} = \frac{\Sigma n_i}{\Sigma n_i(1 - \Omega)^x} \qquad (A)$$

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[1] This research supported by A.E.C. Contract No. AT-(11-1)-407.

[2] D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961).

[3] R. Wolfgang, *et al.*, "Chemical Effects of Nuclear Transformations," Vol. 2, p. 83 and p. 99, International Atomic Energy Agency, Vienna, 1961. This contains references to earlier publications.

[4] J. K. Lee, B. Musgrave and F. S. Rowland, *J. Am. Chem. Soc.*, **82**, 3545 (1960).

[5] J. K. Lee, B. Musgrave and F. S. Rowland, *Canad. J. Chem.*, **38**, 1756 (1960).

[6] F. S. Rowland, J. K. Lee, B. Musgrave and R. M. White, "Chemical Effects of Nuclear Transformations," Vol. 2, p. 67, International Atomic Energy Agency, Vienna, 1961.