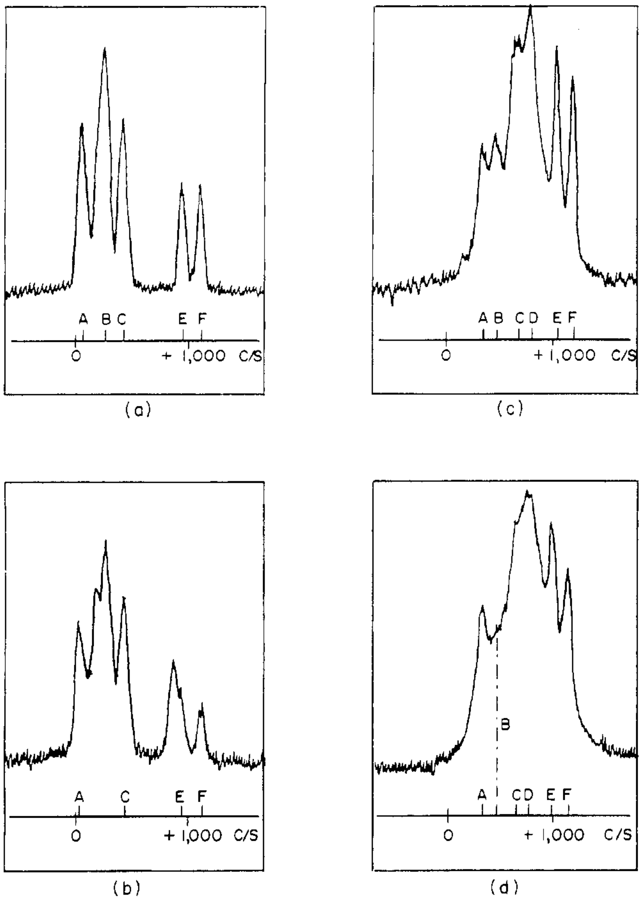

Fig. 1.—^{11}B n.m.r. spectra at 19.3 Mc./sec. of: (a) decaborane (I), (b) 2-bromodecaborane (II), (c) bis-(diethyl sulfide)-decaborane (III), (d) bis-(diethyl sulfide)-2-bromodecaborane (IV). The origin of the frequency scale is the B(OCH$_3$)$_3$ capillary line position. Increasing number corresponds to increasing field (1930 c.p.s. = 100 p.p.m.)

bromodecaborane (IV, m.p. 101°) were synthesized by treating diethyl sulfide with decaborane (I) and 2-bromodecaborane (II), respectively. The ^{11}B n.m.r. spectra of these four compounds, taken at 19.3 Mc./sec., are shown in Fig. 1; the solvent used for I and II was benzene while deuteriochloroform was used for III and IV. A reference spectrum of III in benzene was found to be identical with that determined in deuteriochloroform. The terminal protons of each compound were excited at 60.0 Mc./sec. to decouple successively the various boron nuclei. The area measurements show an intensity ratio of 2:6:2 for the AB:CD:EF regions of spectra c and d.

The decaborane spectrum has been interpreted[3] and the high field doublet was assigned to the two equivalent boron atoms 2 and 4. Spectrum b, previously interpreted,[5] identifies 2-bromodecaborane. The spectral differences of compounds III and IV indicate that the low field doublet of spectrum c is due to borons 2 and 4. In spectrum d, the singlet A is due to the substituted 2 boron and is superimposed on the first part of the doublet of the 4 boron. Inductive arguments based on these spectra may be given to show that the higher field doublet arises from borons 1 and 3. Lines E and F of spectrum c are surprisingly sharp. The same observation[6] in the spectrum of the $B_{12}H_{12}^{-2}$ may be attributed to the high degree of symmetry of its icosahedral structure.[7] In accord with the structure of $B_{10}H_{12}$-(ligand)$_2$ compounds as originally assigned,[1a] we would expect a higher degree of symmetry for borons 1 and 3 than for borons 6 and 9. The similarity of the bonding hybrids[8] between $B_{12}H_{12}^{-2}$ and the 1-B and 3-B borons suggests the same conclusion that the E and F lines of spectrum c correspond to borons 1 and 3. A similar treatment of 1,2,3,4-tetradeuteriodecaborane would add further proof that this assignment is correct.

Acknowledgment.—We thank Mr. G. D. Vickers for obtaining the ^{11}B n.m.r. spectra and acknowledge the partial support of this work by the Office of Naval Research.

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[5] R. Schaeffer, J. N. Shoolery, and R. Jones, *J. Am. Chem. Soc.*, **80**, 2670 1958).

[6] A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **82**, 3228 (1960).

[7] J. A. Wunderlich and W. N. Lipscomb, *ibid.*, **82**, 4427 (1960).

[8] H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (London), **230**, 110 (1955).

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RECEIVED JANUARY 9, 1963

The Covalent Radius of Xenon

Sir:

The evaluation of electronegativities in terms of the "relative compactness" of atoms depends on estimates of "covalent" radii of the "inert" elements.[1] The recent determination of the bond length in xenon tetrafluoride[2] gives the first opportunity to test the validity of these estimates. The "covalent" radius of xenon was earlier determined[1] by a graphical extrapolation of crystal ionic radii, following Pauling, who, however, used "univalent crystal radii" and obtained somewhat different values.[3] The value of 2.09 Å. thus estimated fits exactly the empirical equation relating the "covalent" radii of all the "inert" elements, which was used in determining the radon radius.[4] It is of interest to apply this value to calculate the bond length in XeF_4, for comparison with the observed value.

The electronegativity, measured as the relative compactness of the atoms of the elements, is determined as the ratio of the average electronic density of an atom to that of a hypothetical isoelectronic inert atom.[1] For any of the "rare gas" family this ratio is, of course, 1.00. Since these elements have until recently been considered chemically inert, this value has seemed to have no real significance as an electronegativity.

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[1] R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960.

[2] J. A. Ibers and W. C. Hamilton, *Science*, **139**, 107 (1963).

[3] L. Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

[4] R. T. Sanderson, *J. Inorg. Nucl. Chem.*, **7**, 288 (1958).

However, the recent discovery of fluoride formation by xenon,[5] radon,[6] and krypton[7] suggests that under the circumstances of bond formation, neither electronegativity nor covalent radius of the "inert" elements need remain hypothetical.

According to the principle of electronegativity equalization and related concepts,[1] the electronegativity of XeF_4 is the geometric mean of the values of the component atoms before reaction. This is calculated to be 4.05, using the "compactness" scale of 5.75 for fluorine and 1.00 for xenon. By definition, this electronegativity is also equal to a ratio, r_i^3/r^3, where r is the covalent radius of a *combined* atom in the molecule and r_i the radius of the (usually) hypothetical isoelectronic inert atom. For xenon the inert atom is not hypothetical, and r_i is 2.09 Å. The radius r of xenon in XeF_4 is determined as follows. The electronegativity of XeF_4, 4.05, is equal to $2.09^3/r^3$, or $r = \sqrt[3]{9.13/4.05} =$ 1.31 Å. The radius of fluorine in the same compound is similarly calculated to be 0.81 Å. The radius sum is thus 2.12 Å. In a comprehensive survey of bond lengths,[8] single bonds to fluorine were found to be of length close to 0.92 times the sum of the radii-in-the-compound. This factor times 2.12 equals 1.95 Å., which is in reasonably close agreement with the reported[2] value of 1.92 ± 0.03 Å. The contraction of the xenon radius corresponds to a calculated positive charge of 1.36, and the increase in radius of fluorine to a partial negative charge of -0.34 (electron). In condition of fluorine, this would place XeF_4 between the fluorides of magnesium and aluminum. The fact that these xenon fluorides are quite volatile despite the indicated high polarity of the bonds can be explained in terms of the observation[9] that outer vacant orbitals on the cationic atom appear to be an inherent essential in the usual condensation of metal salts to ionic or polymeric crystals. Such vacancies are relatively unavailable on the xenon.

This bond length calculation assumes a two-electron bond between xenon and fluorine, an assumption which must be regarded with caution since the bonding may be of some other type.[10] However, the promotion of one electron from each of two xenon orbitals to outer d-orbitals, analogous to "expanding the octet" of phosphorus, would create the essentials for the four bonds observed. Furthermore, the presence of the two additional unshared electron pairs on the xenon would reasonably be expected to produce the observed[2] planarity of XeF_4, these pairs then filling the fifth and sixth corners of an octahedron around the xenon. The bond length is at least consistent with that calculated for a two-electron covalent bond. The linearity[5] of XeF_2 could be explained as the result of a trigonal bipyramidal structure with fluorines opposite and the three equatorial positions occupied by the three remaining unshared pairs of electrons of the xenon atom.[10]

A theory is neither validated nor invalidated by one bond length calculation, but the apparent consistency of the earlier selected[1] covalent radius and electronegativity of xenon with the experimental bond length in XeF_4 seems at least worthy of attention. We may await with interest other data which should permit better insight regarding the concepts of electronegativity and partial charge, and perhaps suggest a more conclusive answer to the question of whether covalent radii of the "rare gases" are larger[1,3] or smaller[11] than those of the adjacent halogens. In anticipation of future measurements, the bond lengths in XeF_2 and KrF_4 are here predicted to be close to 2.11 and 1.84 Å., respectively.

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(5) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(6) P. R. Fields, L. Stein, and M. H. Zirin, *J. Am. Chem. Soc.*, **84**, 4164 (1962).

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(8) R. T. Sanderson, *Science*, **114**, 670 (1951).

(9) R. T. Sanderson, *J. Chem. Educ.*, **38**, 382 (1961).

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(11) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952.

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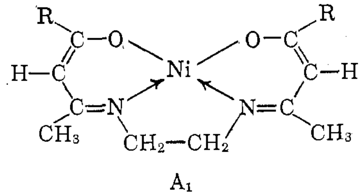
RECEIVED JANUARY 16, 1963

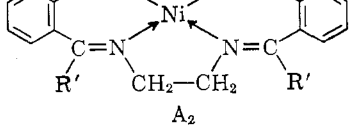
Amine-Catalyzed Condensation of β-Diketones Using a Metal-Chelate Template

Sir:

Compounds of type A_1, A_2 have been prepared by a novel method which consists of the amine-catalyzed reaction of a β-diketone (or related compound) and tetrakis-(ethylenediamine)-μ-dichlorodinickel(II) chloride (B) which serves as a source of ethylenediamine and as a template[1] for the reaction.



A_1



A_2

R = CH_3,C_6H_5
R′ = H,CH_3

It seems significant that the interaction of acetylacetone and B in the absence of pyridine results merely

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(1) For a prior example of a metal-chelate compound functioning as a template, see M. C. Thompson and D. H. Busch, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1960, p. 13N.