96% sulfuric acid over several days at room temperature as evidenced by the unchanged doublet in its n.m.r. spectrum,[14] although it is solvolyzed in aqueous solution under similar conditions. The comparison is not rigorous, since in the case of I a phenyl group not previously conjugated with the double bond is brought into conjugation with the carbonium ion. However, the vast difference in the reactivities of bromoketones I and VII leaves no doubt that the phenyl groups of dicarbonium ion II are exerting a major stabilizing influence. The close similarity in the appearance of the n.m.r. spectra of sulfuric acid solutions of carbonium ion II, acetophenone, benzhydrol, and the diphenylcyclopropenium ion, in spite of evident differences in the importance of phenyl delocalization of the positive charge, suggests that the extent of phenyl delocalization of the positive charge may not be the dominant factor in reversing the order of the chemical shifts in triarylcarbonium ions.[15-17]

Acknowledgment.—We thank the National Science Foundation for support under NSF Grant G-14454.

(14) The n.m.r. spectrum of the corresponding alcohol in 96% sulfuric acid exhibits a singlet at τ = 8.02 p.p.m. and would easily have been detected.

(15) This point is further brought home by an examination of the spectroscopic properties of sulfuric acid solutions of 3,4-dibromo-1,2,3,4-tetraphenylcyclobutene.[3,16] The visible spectrum exhibits a maximum at 482 mμ,[3] similar to that of 11, but with an extinction coefficient of 50,000, less than one-half that of 1I. The n.m.r. spectrum in 1:1 thionyl chloride and fuming sulfuric acid exhibits a multiplet extending from τ = 1.90 to 2.55 of an entirely different appearance from those shown in Fig. 1. These differences can be explained either in terms of a rapidly rearranging monocation (iii) or a dication (iv) in which the phenyl groups are hindered from coplanarity as in the trityl carbonium ion.[17]
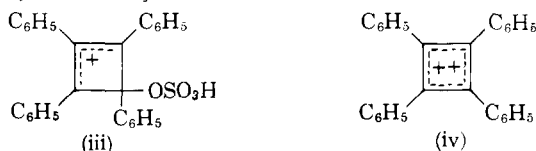
(16) We are grateful to Dr. Freedman for a sample of the dibromide.

(17) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); *J. Chem. Phys.*, **34**, 1460 (1961).

(18) Fellow of the Alfred P. Sloan Foundation.

DEPARTMENT OF CHEMISTRY   DONALD G. FARNUM[18]
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Improved Bond Angle Calculations[1]

Sir:

Recently one of us published a calculation of the bond angles in some six-membered aromatic ring systems containing carbon and nitrogen atoms.[2] The bond angles were obtained by evaluating and minimizing the molecular energy as a function of the internal bond angles with the additional restraint that the sum of the six angles be 720°. Apparently we did not impose any conditions relating the bond angles and distances. It was pointed out to us by Coulson[3] that we might obtain a better agreement with experiment if we restrict the bond angles to those values only that are compatible with hexagons whose sides are equal to the experimental bond distances. This means that we have to impose a second geometrical constraint on the angles in order to ensure that the six vectors having the experimental bond distances as magnitudes and connecting the adjacent nuclei form a closed hexagon. In order to illustrate this geometrical

(1) This work was supported by a grant from the U. S. Army Research Office (Durham) to the University of Pennsylvania.

(2) H. Kim and H. F. Hameka, *J. Am. Chem. Soc.*, **85**, 1398 (1963).

(3) C. A. Coulson, private communication; see also C. A. Coulson, *J. Chem. Soc.*, in press.

constraint we consider pyridine, following the notation of Fig. 2 of ref. 2 and calling the carbon atoms C_β, C_γ, C_δ, etc. We have to impose the condition that C_δ lies directly under N, or, according to Coulson[3]

$$(NC_\beta) \sin \frac{1}{2}\alpha - (C_\beta C_\gamma) \sin \left(\frac{1}{2}\alpha + \beta\right) - (C_\gamma C_\delta) \sin \frac{1}{2}\delta = 0$$

(1)

where $(C_\beta C_\gamma)$ is the experimental distance between C_β and C_γ and (NC_β) and $(C_\gamma C_\delta)$ are similarly defined. For pyrimidine and pyridazine we have to impose similar restrictions on the bond angles; for pyrazine, s-triazine, and s-tetrazine they are automatically fulfilled because of the molecular symmetry. The experimental bond distances in pyridazine are not available so that we took (CC) and (CN) equal to the average values for the other molecules and we chose (NN) in such a way that (CN) is the geometrical average of (CC) and (NN).

The results of the bond angle calculations according to the method of ref. 1 with the inclusion of the geometrical restraint (1) are shown in the last column of Table I. In the first column we have listed the experimental values, insofar as they are available, the second column contains the old results of ref. 2, and the third column shows Coulson's values. The definitions of the angles and the sources of the experimental results may be found in ref. 2.

TABLE I

EXPERIMENTAL AND VARIOUS CALCULATED BOND ANGLES

Molecule	Angle	Exptl.[a]	Kim-Hameka[a]	Coulson[b]	Present
Pyridine	α	117°	110°	115.0°	114.9°
	β	124	121	124.4	125.0
	γ	118.5	122	119.4	119.0
	δ	118	123	117.0	117.0
Pyrimidine	α	115	111	115.0	114.0
	β	128	124	128.7	130.4
	γ	123	125	121.3	121.2
	δ	116	124	118.6	119.1
Pyridazine	α		113	120.1	119.7
	β		124	124.0	124.1
	γ		123	116.9	116.2
Pyrazine	α	115	112	112.6	112.6
	β	122.5	124	123.7	123.7
s-Triazine	α	113	114	114.4	113.8
	β	127	126	125.6	126.2
s-Tetrazine	α	116	115	116.3	115.0
	β	127	130	127.5	130.0

[a] See ref. 2. [b] See ref. 3.

It follows that the inclusion of the geometrical constraint (1) in our calculations improves the agreement between theory and experiment considerably, the mean deviation is reduced from 3.4° to 1.6°. It is interesting to note that this quantity is 1.2° for Coulson's calculations[3] and that the mean deviation between our present results and Coulson's values is only 0.7°.

One is automatically drawn to a comparison between Coulson's method and ours since his results agree about equally well with experiment. It may be argued that Coulson's method is the simpler of the two whereas ours gives more insight into the nature of the various effects determining the bond angles. However, we believe that the two methods should rather be considered as supplementary to one another instead of competing. Coulson's approach shows a very convenient simple way to calculate bond angles and our more detailed considerations seem to justify the various assumptions that were made by Coulson.

Acknowledgment.—Thanks are due to Professor C. A. Coulson, F.R.S., for pointing out the advisability of including the geometrical constraint (1) in the calculations and for sending his theoretical results before publishing them.

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Preparation and Structure of a New Boron Hydride, $B_{20}H_{16}$

Sir:

A new boron hydride, $B_{20}H_{16}$, m.p. 195–197°, has been prepared by slow passage of $B_{10}H_{14}$ and H_2 through an a.c. discharge of 1700 v. between Cu electrodes spaced 16.3 cm. apart.[1] The composition and molecular structure were established by a complete three-dimensional X-ray diffraction study.
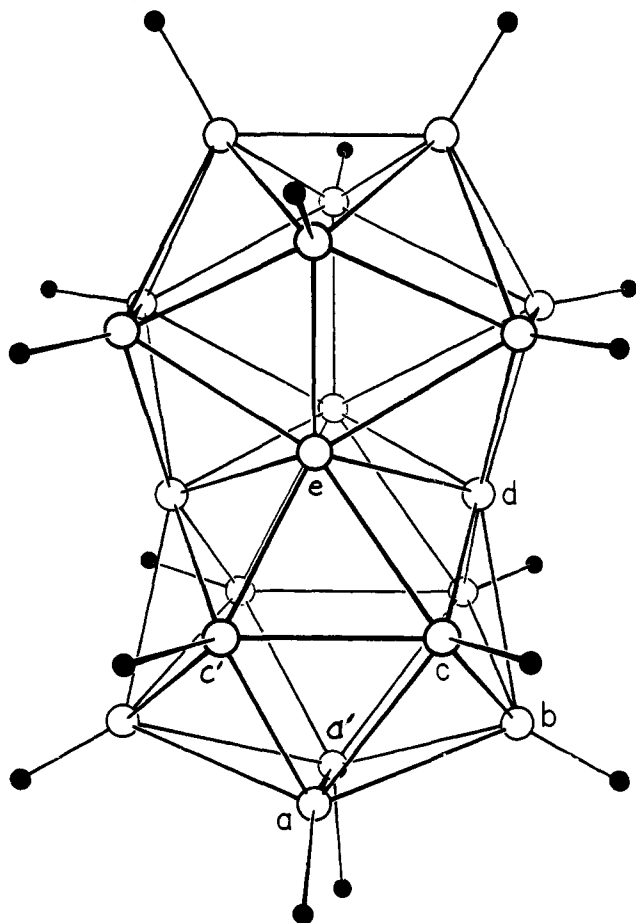

Fig. 1.—Molecular structure of $B_{20}H_{16}$. Bond distances are a–a′ = 1.76, a–b = 1.81, a–c = 1.79, b–c = 1.81, b–d = 1.76, c–c′ = 1.78, c–d = 1.87, c–e = 1.80, and d–e = 1.78, all ±0.01 Å. The primes refer to bonded atoms related by the D_{2d} symmetry, which the molecule has within experimental error.

Beautiful single crystals, easily obtained by sublimation, were shown to be tetragonal in the space group $I4_1/acd$. There are eight molecules in a unit cell having dimensions $a = 9.65$ and $c = 29.64$ Å., and the space group requires molecular symmetry of D_2 or S_4. The intensities were well fitted by placement of the B_{20} unit (Fig. 1) of D_{2d} symmetry of the sites of S_4 symmetry, but not at the sites of D_2 symmetry. All H atoms were located unambiguously, without chemical

(1) R. N. Grimes and W. N. Lipscomb, *Proc. Natl. Acad. Sci.*, **48**, 496 (1962).
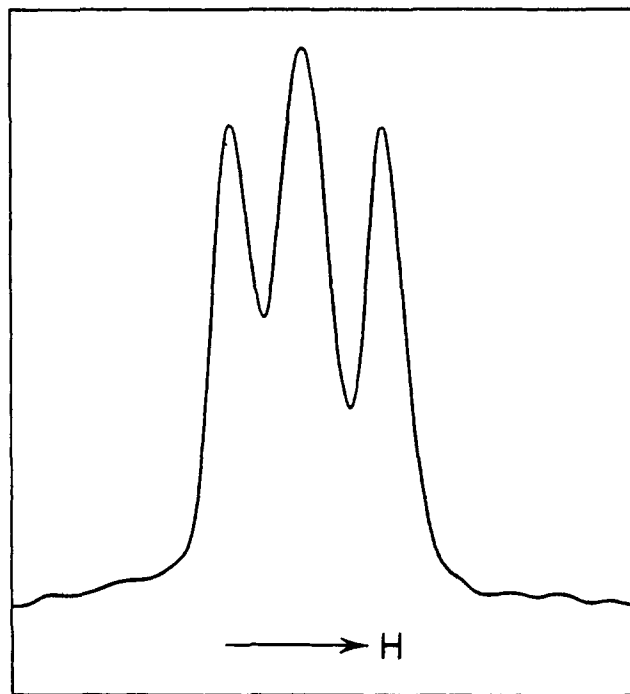

Fig. 2.—B^{11} n.m.r. spectrum of $B_{20}H_{16}$.

assumptions, in three-dimensional electron density maps from which B atoms had been subtracted. The present value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0.143 for the 610 observations.[2]

These results confirm our tentative conclusions[3] based upon the molecular symmetry required by the space group, the crystal density of 1.130 g. cm.$^{-3}$ obtained while the crystal was dissolving rapidly, and the B^{11} nuclear magnetic resonance spectrum (Fig. 2) which suggested B atomic electronic environments more like those in $B_{12}H_{12}^{-2}$ rather than those in $B_{10}H_{14}$, $B_{10}H_{14}^{-2}$, or $B_{10}H_{10}^{-2}$. In particular, the B^{11} n.m.r. spectrum suggests that there are no bridge H atoms, and that some B atoms should not have terminal H atoms. However, the coupling anomaly associated[3,4] with the apex BH_2 unit of B_5H_{11} raised sufficient doubt about the uniqueness of this interpretation of the B^{11} n.m.r. spectrum that we waited until the completion of chemical analysis by three-dimensional X-ray diffraction techniques before reporting this compound and its structure.

Further studies, now in progress, of the reactions of this compound will be reported later. It forms a strongly acid solution upon reaction with water, and, although thermally very stable, is very hygroscopic.

Acknowledgments.—We wish to acknowledge a recent private communication from E. L. Muetterties in which he reports in collaboration with N. E. Miller the independent synthesis, by pyrolysis, of $B_{20}H_{16}$ and its B^{11} n.m.r. spectrum. We also acknowledge support of this research by the National Science Foundation, the Office of Naval Research, and the National Institutes of Health. Assistance of R. N. Grimes and H. A. Beall in the experimental studies is gratefully acknowledged.

(2) If the four largest reflections, which were difficult to correlate to the same scale as the others, are omitted, and if a single parameter correction for secondary extinction is also made, R then becomes 0.107.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(4) L. R. Lavine and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 2087 (1953).

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