Fig. 1.—Schematic energy diagram (in kcal./mole) for reaction of gas phase and solvated *t*-butoxy radicals (dashed lines are energy levels of solvated species).

We obtain evidence on the magnitude of solvent participation in the transition state for hydrogen abstraction processes by reinvestigating[3] the tertiary/primary chloride ratio obtained in the *t*-butyl hypochlorite chlorination of 2,3-dimethylbutane, Table II. Results are striking in that chlorobenzene and acetic acid *reduce* the measured selectivity, apparently through a decrease in the *PZ* factor for *t*-H abstraction, even though the activation energy difference increases. Evidently solvent participation is important and would increase the selectivity of the *t*-butoxy radical were it not for a large entropy loss associated with a highly restricted orientation for attack of a solvated *t*-butoxy radical on a tertiary hydrogen.

TABLE II

t-BUTYL HYPOCHLORITE CHLORINATION OF 2,3-DIMETHYLBUTANE

Solvent	t/p ratio[a] 40°	0°	$E_p - E_t$[b]	log $(PZ)_t/(PZ)_p$
C₆H₆[c]	55.3	88.6	1990	0.36
None[c]	44.4	68.5	1850	.36
C₆H₅Cl	38.4	95.4	3420	−0.79
CH₃COOH	19.5	52.9	4230	−1.66

[a] Relative reactivities (per H) of tertiary and primary hydrogen. [b] Activation energy difference, cal./mole. [c] Data from ref. 3.

The gas phase energetics for β-scission of the *t*-butoxy radical have been estimated[8] as E_a = 13 kcal., ΔH = 4.7 kcal. Assuming 3 kcal. stabilization of the transition state for hydrogen abstraction in solvents such as acetic acid (which seems a minimum value in view of the changes in $E_p - E_t$ in Table II) we can construct the energy diagram for *t*-butoxy radical reactions shown in Fig. 1. This indicates a stabilization of the transition state for β-scission of 7–8 kcal., a plausible value for strong hydrogen bonding, and we have used the same value for the ground state radical.

More extensive data and discussion on these systems will be published elsewhere, but it is evident that solvent effects in *t*-butoxy radical reactions are much more pronounced than had been realized previously.

(8) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959)

(9) National Science Foundation Predoctoral Fellow, 1961–1963.

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Configuration of the Porphine Skeleton in Unconstrained Porphyrin Molecules[1,2]

Sir:

The classical X-ray diffraction analyses of crystalline structure for the phthalocyanines[3] are generally cited in support of a naturally planar configuration for the porphine skeleton in porphyrins, whereas two recent analyses of nickel etioporphyrin-I[4] and copper tetraphenylporphine[5] assign nonplanar configurations to the porphine skeleton in the crystalline materials. Application of relevant theory to the accurate stereochemical data presented below for tetraphenylporphine provides a mutual accommodation of the earlier observations, and other general conclusions of interest.

Apart from obvious differences at the molecular center, tetraphenylporphine is isostructural with the copper derivative,[5] and we employ an analogous notation for the asymmetric grouping in the tetragonal space group I42d. The four-molecule cell has a = 15.125 ± 0.025, c = 13.94 ± 0.02 Å. The required molecular symmetry (*vide infra*) is $S_4 - \bar{4}$. The 892 observed $\{hkl\}$ intensities correspond to a 91% yield with Cu Kα radiation. Least squares refinement which utilized anisotropic thermal parameters, followed by difference synthesis, furnish the stereochemical data of Fig. 1. Standard deviations for bond parameters
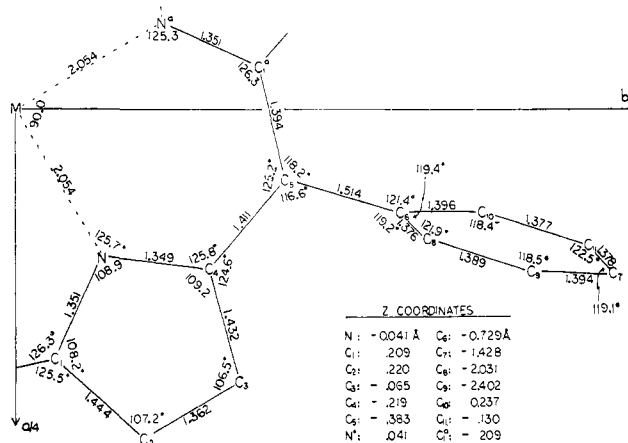

Fig. 1.—Diagram in true projection along the $\bar{4}$ axis (c of the crystal) of a portion of the tetraphenylporphine skeleton (and of the appropriate metal derivative). The skeletal ruffling is to negative z in the first and third quadrants, to positive z in the second and fourth.

within the porphine skeleton are 0.006–0.008 Å. for lengths, *ca.* 0.4° for angles; mostly larger and more variable values apply to the phenyl group. With two less satisfactory peripheral exceptions, quantitatively plausible positions for hydrogen atoms, including the "half-atoms" attached to nitrogen, are directly indicated by the difference maps.

Maximum deviations from planarity within the porphine skeleton occur at methine carbon; the z-coordinate alternates between -0.38 and $+0.38$ Å. for each rotation of 90° about c. Besides the pyrrole and benzene rings, the following key groupings are flat within experimental accuracy: $C_6C_5C_8C_{10}$, $C_1{}^aC_5N{}^aC_2{}^a$, $C_4C_5NC_3$, $C_5C_6C_1{}^aC_4$. The angle between the planes of

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 236 (1940).

(4) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963).

(5) E. B. Fleischer, *ibid.*, **85**, 1353 (1963).

$C_5C_6C_1{}^aC_4$ and the phenyl group is $81.5°$, with C_5, C_6 and C_7 on the line of intersection. The planes of C_5C_6-$C_1{}^aC_4C_7$ and of a pyrrole ring are inclined, respectively, $14.2°$ and $12.0°$ to (001). The principal circumstances adverse to ideal π-bonding are pinpointed by noting that, in order to achieve exact planarity with $C_5C_6C_1{}^aC_4$, the pyrrole rings of Fig. 1 would need to be rotated about the bonds $C_5-C_1{}^a$ and C_5-C_4 by, respectively, $6.5°$ and $13.6°$.

The grouping $NC_4C_5C_1{}^aN^a$ is not planar and the formally completed chelate ring $MNC_4C_5C_1{}^aN^a$ is puckered. Bond angles at carbon (and at nitrogen) substantially exceed the ideal value of $120°$ for σ-bonding in trigonal hybridization. The urge toward reduction of these bond angles through stronger puckering is subject to quasi-rigid constraints set by the character of the pyrrole ring, e.g., the external angles at $C_1{}^a$ and C_4 should remain sensibly equal and cannot be much less than $125°$. There remain quite general grounds, with support from the examination of various models, for concluding that a planar configuration cannot minimize strain for σ-bonding. Inasmuch as the restoring forces associated with π-bonding are zero for initial deformation, one concludes also that some departure from planarity in the porphine skeleton—in *seeming* disproportion with the small energetic gain—is inevitable in a free molecule.

A ruffling of the skeleton in agreement with $\bar{4}$ is plausible for a metal derivative in which $M-N < 2.05$ Å. (cf., ref. 5), with a small energy barrier to reflection of configuration through the mean plane. At sufficiently high temperature, perhaps even at $300°K$., the skeleton should behave as if the configurational potential energy had a single, very broad minimum. The extraordinary deformability normal to the mean plane thus implied finds support in the highly anisotropic thermal parameters of our study. One concludes that, with little energetic prejudice, the skeleton either can simulate exact planarity[3] or display considerable ruffling,[5] as the environment demands.

A convex form (C_4 or C_{4v} symmetry) of the skeleton becomes plausible with longer $M-N$ bonds, by allowing the metal atom to lie far enough outside the plane of the four nitrogens to take care of the added dimensional constraint. This configuration, moreover, could be induced by the additional coordination of an externally constrained ligand to M. The high spin Fe^{+2} and Fe^{+3} derivatives are outstanding candidates for such configurations. Thus Kendrew's[6] observation that, in myoglobin, the iron atom lies more than 0.25 Å. out of the mean plane of the heme group is interpretable in simple fashion.

(6) J. C. Kendrew, *Science*, **139**, 1259 (1963), who mentions also that D. Koenig, The Johns Hopkins University, has observed the same phenomenon through structure analysis of hemin.

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On the Crystal Structure of AlB_{10}

Sir:

The higher aluminum borides AlB_{10}, AlB_{12} and its polymorphs are distinct from other higher metal borides in that the former combine exact stoichiometric chemical formulas with an anomalous number of formula units per crystallographic unit cell. Despite extended efforts, no crystal structure of any of the higher aluminum borides has thus far been solved.

We have found a structure for AlB_{10} from an X-ray study of a single crystal prepared earlier at this laboratory.[1] The symmetry is orthorhombic, with $a = 8.88$,

$b = 9.10$ and $c = 5.69$ Å.; chemical analysis and density measurements indicated 5.2 AlB_{10} formula units per unit cell.[1] The space group is B $2/b$ $2_1/m$ $2/m$, from which four or eight formula units are to be expected.

The crystal structure found is based on an icosahedral (12-grouping) arrangement, consisting of four boron icosahedra and four inter-icosahedral boron atoms per unit cell. Thus 52 boron atoms are located, in agreement with the chemical analysis. Statistical distribution over several sites must be assumed for the aluminum atoms, which may or may not substitute for boron atoms.

An icosahedral packing of boron atoms was first recognized in $B_{12}C_3$[2] and has also been reported for tetragonal boron,[3] in low-temperature α-rhombohedral boron,[4] and recently for high-temperature β-rhombohedral[5] boron. It is also favored from some theoretical aspects.[6]

X-Ray analysis of AlB_{10} has been restricted so far to the (100) and (001) projections. The unit cell is thereby reduced to 0.25 and 0.5, respectively, of its full size, thus significantly decreasing the number of parameters to be determined. In (100), therefore, one icosahedron is expected, which was revealed and oriented by applying convolution molecule methods[7] to the Patterson projection and confirmed by Fourier transform methods using the weighted reciprocal lattice. Fourier and least squares calculations of the icosahedron alone in this projection resulted in an R-factor of 28.5%.

By applying the convolution molecule method to the (001) Patterson projection, the two expected icosahedra were located and their relative orientation and translation parameters determined. Working with icosahedra alone and omitting inter-icosahedral atoms, the combined (100) and (001) projections gave an R-factor of 29.3%.

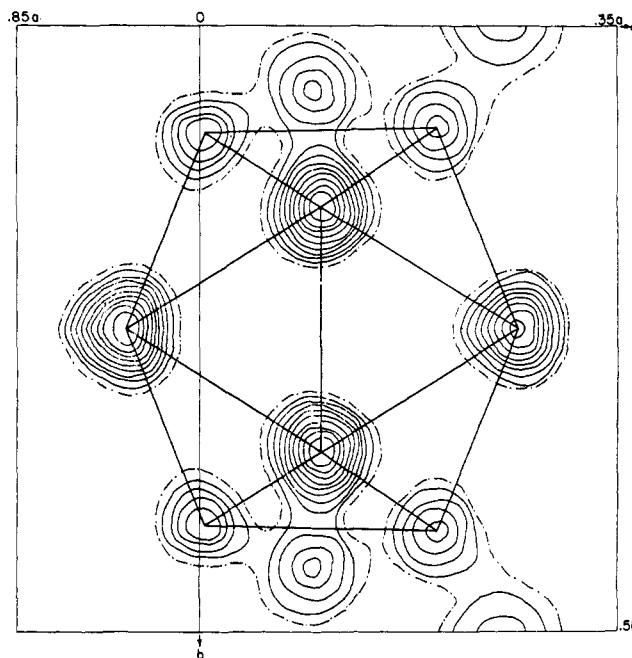Using the signs of the least square refinement, Fourier calculations revealed additional peaks, upon

Fig. 1.—Electron density projection of AlB_{10} on (001).

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(2) H. K Clark and J. L. Hoard, *J. Am. Chem. Soc.*, **65**, 2115 (1943).
(3) J. L. Hoard, R. E. Hughes and D. E. Sands, *ibid.*, **80**, 4507 (1958); cf. J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).
(4) L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, *ibid.*, **80**, 2592 (1958); B. F. Decker and J. S. Kasper, *Acta Cryst.*, **12**, 503 (1959).
(5) R. E. Hughes, C. H. L. Kennard, D. B. Sullenger, H. A. Weakliem, D. E. Sands and J. L. Hoard, *J. Am. Chem. Soc.*, **85**, 361 (1963).
(6) W. N. Lipscomb and D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).
(7) W. Hoppe, *Z. Elektrochem.*, **61**, 1076 (1957).