

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 reinvestigating³ 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	40°	<i>i/p</i> ratio ^a		log (PZ) _t /(PZ) _p
		0°	$E_p - E_t^b$	
C ₆ H ₆ ^c	55.3	88.6	1990	0.36
None ^c	44.4	68.5	1850	.36
C ₆ H ₅ Cl	38.4	95.4	3420	-0.79
CH ₃ COOH	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 estimated⁸ as $E_a = 13$ kcal., $\Delta H = 4.7$ 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)

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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 phthalocyanines³ are generally cited in support of a naturally planar configuration for the porphine skeleton in porphyrins, whereas two recent analyses of nickel etioporphyrin-I⁴ and copper tetraphenylporphine⁵ 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 $I4_2d$. The four-molecule cell has $a = 15.125 \pm 0.025$, $c = 13.94 \pm 0.02$ Å. The required molecular symmetry (*vide infra*) is $S_4 - \bar{4}$. The 892 observed $\{hkl\}$ intensities correspond to a 91% yield with Cu K α 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

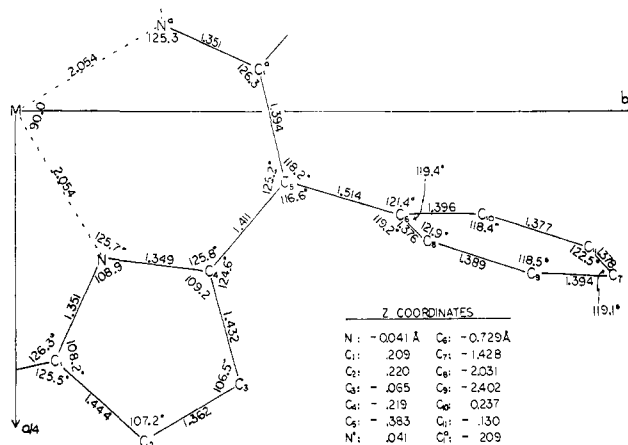


Fig. 1.—Diagram in true projection along the $\bar{4}$ axis (c of the crystal) of a portion of the tetraphenylporphine skeleton (and of the appropriate metal derivative). The skeletal ruffling is to negative z in the first and third quadrants, to positive z in the second and fourth.

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: C₆C₅C₈C₁₀, C₁²C₅N⁴C₂⁸, C₄C₅NC₃, C₅C₆C₁⁴C₄. The angle between the planes of

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(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).