# Additions and Corrections

**Some Very Rapid Reactions of Porphyrins in Aqueous Solution** [*J. Am. Chem. Soc.*, **98,** 1908 (1976)]. By ROBERT F. PASTERNACK,* NORMAN SUTIN,* and DOUGLAS H. TURNER, Departments of Chemistry, Ithaca College, Ithaca, New York 14850, Brookhaven National Laboratory, Upton, New York 11973, and University of Rochester, Rochester, New York 14627.

Table I: The values of $k_{-1}$ and $k_2$ presented in Table I were obtained from the experimental values of $k_1$ and $k_{-1}/k_2$ subject to the constraints that $k_1/k_{-1} \leq 4 \times 10^{-2}$ (otherwise a significant concentration of the nonplanar free-base form would be present) and $k_2 \leq 5 \times 10^{10}$ $M^{-1}$ $s^{-1}$ (which is a reasonable upper limit for proton addition to the nonplanar free-base form under the conditions used).

**Synthesis of Trichloroacetamido-1,3-dienes. Useful Aminobutadiene Equivalents for the Diels–Alder Reaction** [*J. Am. Chem. Soc.*, **98,** 2352 (1976)]. By LARRY E. OVERMAN* and LANE A. CLIZBE, Department of Chemistry, University of California, Irvine, California 92664.

The stereochemical assignment for the major diene (kinetic preference 98:2) formed from thermolysis of the trichloroacetimidic ester of 3-butyn-2-ol is incorrect in the original communication. The diene thus produced is (*Z*)-1-trichloroacetamido-1,3-butadiene. This stereochemical assignment was obvious ($^1H$ and $^{13}C$ NMR, UV) when both stereoisomers became available. Treatment of the kinetically produced cis isomer with triethylamine (0.2 M in dioxane, 110 °C, 30 min) yielded an 85:15 equilibrium mixture of the trans and cis isomers, respectively. Geometrical isomerization also occurs in dioxane at 110 °C in the absence of triethylamine, although much more slowly. As a result, the Diels–Alder reactions reported in eq 2, in fact, do involve primarily the cycloaddition of the trans isomer. The preformed trans isomer, however, is more reactive than would be indicated in eq 2. For example, (*E*)-1-trichloroacetamido-1,3-butadiene reacts cleanly with acrolein within 4 h at 110 °C to afford **7** (95% isolated yield, a 5:1 mixture of cis and trans stereoisomers). Details of the stereochemical assignments and the mechanistic implications of the observed kinetic preference for forming the less stable cis isomer will be discussed in the subsequent full paper.

**Molecular Orbital Studies of the Protonation of the Methylanisoles** [*J. Am. Chem. Soc.*, **98,** 4061 (1976)]. By RAYMOND S. GREENBERG, MAURICE M. BURSEY,* and LEE G. PEDERSEN, William Rand Kenan, Jr.,* Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514.

A geometry error for the neutrals has been corrected. Energy values should be: *o*-methylanisole, −378.884 38 au; *m*-methylanisole, −378.885 14; *p*-methylanisole, −378.884 21. The uncorrected proton affinities, by comparison with the energies of the most stable protonated forms, are 245.3, 249.7, and 246.7 kcal/mol, respectively. As the text indicates, these values must be expected to be larger than experimental values. We thank Professor Warren J. Hehre for pointing out the discrepancy in our original results.

**Application of $^{13}C$ Nuclear Magnetic Resonance Spectroscopy to the Analysis of Charge Distribution Patterns in Unsaturated Carbonyl-Containing Compounds** [*J. Am. Chem. Soc.*, **98,** 4571 (1976)]. By MELANIE J. LOOTS, LINDA R. WEINGARTEN, and RONALD H. LEVIN,* Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138.

S. Berger and A. Reiker [*Chem. Ber.*, **109,** 3252 (1976)] have recently reversed their earlier $^{13}C$ NMR assignments for the two olefinic carbon atoms in *o*-quinone. Therefore, the chemical shifts for C(4) and C(6) for *o*-quinone, presented in Table III of our paper, should be interchanged. The corresponding annulenone correction factors now become +6.9 and +8.8, respectively, and the predicted shifts in Chart II for the parent [5]annulenone become 143.8 [C(2)] and 117.5 [C(4)]. As the *o*-quinone chemical shifts have simply been interchanged, there is no effect upon $Z_{\Sigma}{}^{\pi}$ for cyclopentadienone.

**Nuclear Magnetic Resonance in Pulse Radiolysis. Chemically Induced Dynamic Nuclear Polarization** [*J. Am. Chem. Soc.*, **98,** 6067 (1976)]. By A. D. TRIFUNAC,* K. W. JOHNSON, and R. H. LOWERS, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

The caption for Figure 1 on p 6067 is incorrect. The correct caption is:

**Figure 1.** Pulse radiolysis of mixtures of methanol and sodium acetate in $D_2O$: acetate 2.44 M (A–E); methanol 0.10 M (A), 0.25 M (B), 0.40 M (C), 0.84 M (D), 1.98 M (E).

**Hydration of $NH_4F$** [*J. Am. Chem. Soc.*, **98,** 6820 (1976)]. By PETER KOLLMAN* and IRWIN KUNTZ, Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143.

After submission of this paper, some relevant information has come to our attention. J. O. Noell and K. Morokuma ("A Fractional Change Model in the MO Theory and Its Application to Molecules in Solutions and Solids", *J. Phys. Chem.*, **80,** 2675 (1976); this paper has a more detailed description of the methodology of ref 11 as well as more applications) pointed out that it is important to consider N···F variations in the distance in comparing the energies of the neutral H-bond $H_3N$···HF and the ion pair $H_3N^+$–H···$F^-$. We agree, but feel that our use of a fixed rather long ($R$ = 2.65 Å) N–F distance, optimum for the neutral H-bonded structure will, like our neglect of correlation contributions and the neglect of three-body terms (see last part of section C), make it *harder* to form the *ion pair* compared to shorter N–F distances. For example, using the data from Figure 5 of ref 11 ($r$(H–F) = 1.0 Å is the "neutral" species and $r$(N–H) = 1.1 Å is "ion pair"), at $R$(N–F) = 2.6 Å, the energy difference (ionic–neutral) is about 7 kcal/mol; at $R$(N–F) = 2.4 Å, this difference is only 3 kcal/mol. The relatively crude basis set used here will, compared to a more accurate basis, have an error of the opposite sign (easier to form ion pair). The error introduced by lack of variation of the N–F distance is similar to the correlation errors, many-body errors, basis-set errors, or the necessarily limited search of the other geometrical variables for the $NH_4F$ hydrate; this restriction will tend to make the transition from neutral → ionic occur at a *larger* hydration number than it would if one varied $R$(N···F). Whether the proton potential has a single or double well (Figure 1) will, on the other hand, be sensitive to variation of $R$(N···F) so our calculations cannot be taken as evidence for the "existence" of a double-well po-