tracted with pentane. The pentane layer was separated, washed 3 times with water, and dried over anhydrous magnesium sulfate:sodium bicarbonate (1:1). Evaporation of the solvent under reduced pressure gave white crystals of the crude 2,6-dichloro-4-methoxybenzyl bromide (1.41 g, 5.22 mmol). Diethyl acetamidomalonate (1.09 g, 5.0 mmol) was added to a solution of sodium (0.21 g, 9.1 mmol) in ethanol (40 mL). After 5 min, the benzyl bromide was added and the solution was stirred for 18 h. The reaction mixture was acidified and then poured into water and methylene chloride. After shaking, the organic layer was separated and dried over magnesium sulfate. Evaporation of the solvent gave compound **6b** as a yellow oil which was crystallized from ether (1.17 g, 2.88 mmol, 53%): mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 6 H, J = 7 Hz, ester CH_3), 1.97 (s, 3 H, amide CH_3), 3.77 (s, 3 H, OCH_3), 3.91 (s, 2 H, Ar CH_2), 4.25 (m, 4 H, ester CH_2), 6.42 (br s, 1 H, NH), 6.84 (s, 2 H, Ar H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 13.9, 23.2, 33.5, 55.7, 62.5, 65.6, 114.6, 123.8, 137.4, 158.9, 167.9, 169.1; MS, m/z (relative intensity) 405 (M^+, 3), 370 (M – Cl, 3), 332 (M – $CO_2CH_2CH_3$, 3), 311 (M – Cl – CH_3CONH_2, 15), 290 (M – $CO_2CH_2CH_3$ – CH_2CO, 11), 189 (100). The compound showed a single component upon analysis by TLC in two solvents (chloroform, R_f 0.15; ether, R_f 0.85). Exact mass 405.0756, calcd for $C_{17}H_{21}{}^{35}Cl_2NO_6$ 405.0746.

2,6-Dichloro-DL-tyrosine (1b). The diester **6b** (0.79 g, 1.94 mmol) was refluxed in 48% hydrobromic acid for 24 h. After cooling, the acid was evaporated under reduced pressure, and the residue was dissolved in water. The solution was neutralized with 1 N sodium hydroxide, and it was applied to a column of Dowex-50 (H^+). The column was washed with water, and it was eluted with 1 N ammonium hydroxide. The eluate was concentrated to dryness, and the residue was recrystallized from water to give pure **1b** (0.288 g, 0.91 mmol, 47%), mp 272–274 °C dec; ^{1}H NMR (D_2O-NaOD) δ 2.95 (dd, 1 H, J = 14 Hz, 9 Hz, β-CH_2), 3.12 (dd, 1 H, J = 14 Hz, 6 Hz, β-CH_2), 3.53 (dd, 1 H, J = 9 Hz, 6 Hz, α-CH_2), 6.60 (s, 2 H, Ar-H_2); ^{13}C{^{1}H} NMR (D_2O-NaOD) δ 35.4, 56.2, 118.5, 118.6, 135.3, 166.3, 182.5.

Analysis: C, 40.60; H, 4.26; N, 5.38. Calcd for $C_9H_9Cl_2NO_3 \cdot H_2O$: C, 40.32; H, 4.14; N, 5.22.

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Registry No. **1a**, 94278-64-5; **1b**, 94294-08-3; **4b**, 94278-65-6; **5a**, 79538-27-5; **5b**, 86111-47-9; **6a**, 94278-66-7; **6b**, 94278-67-8; 2,6-difluoro-4-methoxybenzyl bromide, 94278-68-9; diethyl acetamidomalonate, 1068-90-2; 3,5-dichloroanisole, 33719-74-3; 2,6-dichloro-4-methoxybenzoic acid, 94278-69-0; 2,4-dichloro-6-methoxybenzoic acid, 94294-09-4; methyl 2,4-dichloro-6-methoxybenzoate, 94294-10-7; 2,6-dichloro-4-methoxybenzyl bromide, 94278-70-3.

The Structure of *N*-(2-Ammonioethyl)carbamate in Solution

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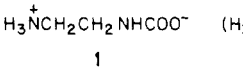
N-(2-Ammonioethyl)carbamate, the solid equimolar adduct of ethylenediamine and CO_2, has been known at least since 1900.[1] In 1951, Katchalski et al.[2] provided evidence that in solution the compound could exist as either a monomolecular zwitterion (**1**) or as a disalt (**2**).



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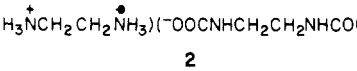

2

Thus, diazomethane in ether was found to react with the solid carbamate to yield a solution containing the monomethyl ester from **1** as well as the dimethyl ester and free ethylenediamine from **2**; they also reported that calcium hydroxide added to an aqueous solution of the carbamate yielded a precipitate which was identified as the calcium salt of the dicarbamate anion.

Subsequent workers have confirmed that alkaline aqueous solutions contain both **1** and **2**. Jensen and Christensen[3] showed that amyl alcohol extracted free ethylenediamine (from **2**) from solutions of the carbamate in 1 M NaOH. Frahn and Mills[4] found two spots, corresponding to monocarbamate and dicarbamate anions, in paper electrophoresis of solutions of ethylenediamine in 0.1 M NaOH after exposure to CO_2. Frank[5] has used an NMR technique to demonstrate the existence of both **1** and **2** in aqueous solutions. The quantitative results of these measurements, however, have been discordant. Katchalsky et al. estimated that their solutions contained about equal weights of **1** and **2**, while Jensen and Christensen reported much smaller proportions of dicarbamate as determined by their procedure. Frank found amounts of **2** varying from 15 to 58 mol % in solutions of different preparations.

Recent X-ray crystallographic studies in this laboratory[6] have shown that solid *N*-(2-ammonioethyl)carbamate prepared in a variety of ways is always composed solely of **1** (although two crystalline polymorphs exist, with orthorhombic and monoclinic unit cells, respectively). Accordingly, it appears that **2** must be formed during or after dissolution of the solid. In the present work ^{13}C NMR has been used to study this process.

Obtaining satisfactory (natural abundance) ^{13}C NMR spectra of *N*-(2-ammonioethyl)carbamate required concentrated solutions in D_2O. Preliminary measurements showed that the number, position, and intensity of lines in the aliphatic carbon region varies with concentration and pH of solutions, presumably due to shifts in protonation equilibria. On addition of strong base (KOD), however, the shifts became reproducible and lines were fairly well resolved; Frank[5] found the same to be true for proton NMR spectra.

Four aliphatic C lines are observed. By comparison with spectra of ethylenediamine and dipotassium ethylenedicarbamate under the same conditions, those at 43.9 ppm (relative to tetramethylsilane) and 42.5 ppm can be assigned to the methylene carbons in ethylenediamine and the dicarbamate anion, respectively. Those at 41.8 and 44.5 ppm, therefore, are associated with the two different methylene carbons in the monocarbamate **1**.

When the solid carbamate was dissolved in ice-cold alkali solution, and the spectrum recorded immediately with the sample maintained at 0 °C, only the monocarbamate lines were present. Very slow conversion to the dicarbamate occurred on storage of the alkaline solution at 0 °C; thus after 46 h the relative line intensities indicated 3.6 mol % of dicarbamate. At room temperature, the reaction is much faster; after 4 h ca. 29 mol % of dicarbamate was observed. On the other hand, solutions of the carbamate in water at the "natural" pH (8.4), or made only slightly alkaline (0.5 M ethylenediamine, pH 9.0), showed no more than ca. 5% dicarbamate after room temperature storage for up to 1 week.

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If *N*-(2-ammonioethyl)carbamate solutions are stored in open containers or purged with nitrogen, the pH rises. This implies that in aqueous solutions without added acid or base the equilibria (eq 1 and 2) are established. On the

$$H_3^+NCH_2CH_2NHCOO^- \rightleftharpoons CO_2 + H_2NCH_2CH_2NH_2 \quad (1)$$

$$H_2NCH_2CH_2NH_2 + H^+ \rightleftharpoons H_3^+NCH_2CH_2NH_2 \quad (2)$$

basis of the pK values,[7] we may estimate that in the pH range 8–9, at least 90% of the ethylenediamine is protonated. Under these conditions, there is little tendency for the formation of dicarbamate. If the pH is raised sufficiently, however, the zwitterion is deprotonated

$$H_3^+NCH_2CH_2NHCOO^- + OH^- \rightarrow H_2NCH_2CH_2NHCOO^- + H_2O$$

and the reaction to form dicarbamate can occur.

Experimental Section

N-(2-Ammonioethyl)carbamate was prepared by passing CO_2 into a solution of ethylenediamine (Eastman) in anhydrous methanol cooled in an ice bath. The resulting precipitate was filtered and dried in vacuum. Elemental analysis was satisfactory; the X-ray diffraction pattern was that of the orthorhombic polymorph. Dipotassium ethylenedicarbamate was prepared as described by Frank;[5] elemental analysis was satisfactory.

NMR spectra were obtained on either a Varian XL-200 or XL-300 spectrometer, operating at 50.3 or 75.4 MHz, respectively, for ^{13}C. All spectra were measured on samples containing 1.04 g (10 mmol) of the carbamate dissolved in 1.1 mL of 40% KOD in D_2O (Merck) plus 2.8 mL of D_2O (or $D_2O + H_2O$), with 0.1 mL of dioxane added as internal standard. Gated decoupled excitation with 10-s pulse delay, together with the addition of 0.1 M disodium (diethylenetriaminepentaacetato)chromate(III) hexahydrate as a relaxation reagent,[8] was used in attempting to obtain quantitative spectra. While these measures sufficed for quantitation of spectra of reference compounds, base-line resolution was not achieved between the carbamate peaks, and their spectra were therefore only semiquantitative.

Aging experiments without added strong base were performed by dissolving the carbamate in 1.5 mL of aqueous solution in a small screw-cap vial, which was allowed to stand tightly capped at room temperature for the desired period. The contents of the vial were then transferred to an NMR tube containing the rest of the ingredients noted above, and which had been pre-cooled in an ice–salt bath at −20 °C.

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Registry No. 1, 109-58-0; 2, 82357-56-0; ethylenediamine, 107-15-3.

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A Novel Synthesis of Triple-Deckered Triporphyrin

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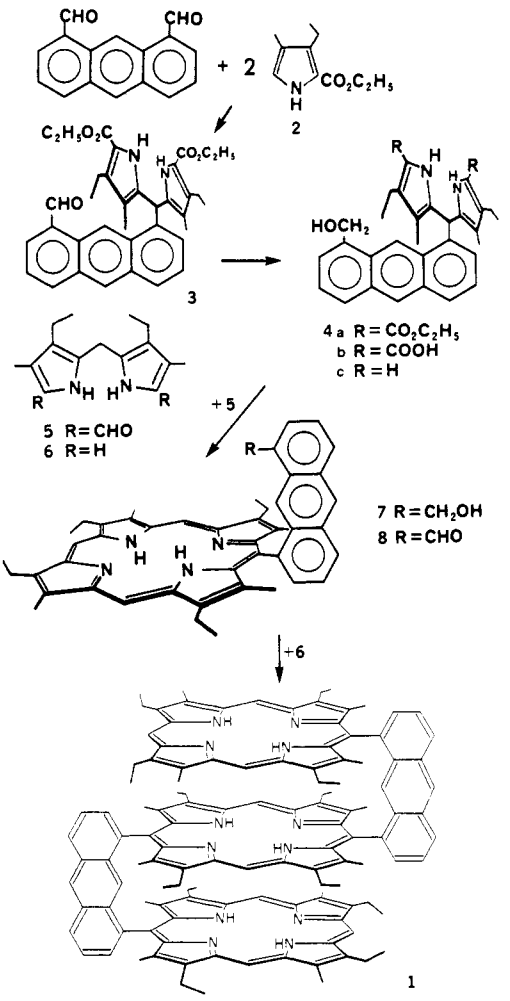
The structure of the primary electron-donor–acceptor complex in reaction centers as well as the molecular events involved in the electron-transport processes remain to be the central questions in photosynthesis. Many attempts have been made to model the light-driven charge separation step using porphyrin and chlorophyll molecules with varying degrees of success.[1-3] A critical element which often is difficult to control in synthetic models is the geometry and distance that separates the donor and acceptor. Furthermore, there has been substantial evidence indicating that the primary donor in the bacterial (also green plant) reaction center may involve dimeric porphyrinoid pigments.[1] Therefore an accurate model system perhaps should contain at least three components, e.g., a chlorophyll dimer in association with a Mg-free pheophytin. Boxer and Buck have indeed linked a difunctionalized chlorophyll to a chlorophyll and a pheophytin via ester groups.[4] Such a linear arrangement was unavoidably too flexible to allow the singly linked trimer to assume any well-defined geometry. Wasielewski et al.[5] more recently synthesized a stacked porphyrin trimer using doubly linked coproporphyrin I and diametrically substituted porphyrin dialcohol. However, because of the C_{2h} symmetry of the porphyrin monomers, the resultant trimer was a mixture of three diasteromers. In order to avoid the shortcomings

Scheme I



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