(2) The absorption spectra of solutions of lithium, potassium[5] and cesium are identical with those for sodium solutions of similar concentration within the limits of experimental uncertainty, which for the former solutions was ± 10%. Hence the spectra of the M and M_2 species (in the visible and infrared) do not depend upon the particular metal.

(3) Gunn and Green[7] have found that the apparent molar volume of lithium in ammonia 0° is practically constant at 50 ml./mole from 0.02 to 0.99 *M*. For sodium, the apparent molar volume changes only from 56.3 to 58.6 ml./mole from 0.0093 to 0.34 *M*. The latter data are inconsistent with some preliminary data of Evers and Filbert[8] which indicate a marked minimum in the volume–concentration curve for sodium at 0.03 *M*. However, until the latter findings are confirmed, we shall favor the former data and therefore conclude that the partial molal volumes of $M^+ + e^-$, of M, and of $^1/_2\ M_2$ are nearly the same.

(4) Nuclear magnetic resonance data[9] are available only above 0.05 *M*. In the range 0.05 to 0.2 *M* the unpaired electron spin density on the sodium nuclei is only about 0.1% of that expected for isolated sodium atoms. The n.m.r. shift for nitrogen is rather large and indicates that an appreciable fraction of the unpaired electron spin density extends into the ammonia solvent regions. Since in this concentration range the concentration ratio of M to e^- is not small, the electron spin density on the metal atom nucleus must be small for the species M.

This evidence, taken as a whole,[10] is quite inconsistent with the Becker, *et al.*, model where the volumetric and spectral properties of ($e^- + M^+$), M, and $^1/_2\ M_2$ would be expected to differ widely. Douthit and Dye[6] and Evers[11] have pointed out that if the monomer were simply an ion-pair consisting of an ammoniated metal ion and an ammoniated electron, the constancy of the spectra in the dilute range could be explained. They make no such proposal for the dimer. However, our spectral data require a new picture for M_2 as well. We picture the M_2 species as a quadrupolar ionic assembly of $2e^- + 2M^+$ in which there is little distortion of either the ammoniated electrons or ammoniated metal ions. Presumably the electrons and ions are held in a square or rhombic configuration. The probability density for the electron in the solvated e^- species extends with decreasing intensity through several solvent layers.[12] Thus the wave functions for the two e^- in M_2 will overlap significantly and it is reasonable that the singlet state should be lower in energy than the triplet by more than *kT*. Also a small electron density at the sodium nucleus in the ion pair (M) species is to be expected. Both the volume and the 1s–2p spectral frequency depend primarily on the cavity size for the solvated electron. Thus, if this cavity retains its size through ion pair and quadruplet formation, the results cited in (1), (2), and (3) above become understandable.

Presumably the solvated electron retains its structure in further polymeric species (*e.g.*, M_4) which probably form in more concentrated solutions. However, in highly concentrated solutions, one should expect that the nature of the ammoniated electrons would change if for no other reason than that there are insufficient ammonia molecules to properly coördinate both the metal ions and the electrons. We believe the deviations from Beer's law which occur in sodium solutions more concentrated than 0.03 *M* indicate the formation of high polymers with incipient metallic bonding.

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(5) We find no evidence for a negative deviation from Beer's law for potassium as reported by Douthit and Dye.[6]

(6) R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, **82**, 4472 (1960).

(7) S. R. Gunn and L. G. Green, *J. Chem. Phys.*, **36**, 363 (1962).

(8) E. C. Evers and A. M. Filbert, *J. Am. Chem. Soc.*, **83**, 3337 (1961).

(9) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **26**, 1517 (1957); J. Acrivos and K. S. Pitzer, unpublished data.

(10) W. E. Blumberg and T. P. Das (*J. Chem. Phys.*, **30**, 251 (1959)) treat the n.m.r. data on the basis of the Becker, *et al.*, model with reasonable agreement. The fit is strained, however, and would be easier on our model.

(11) E. C. Evers, *J. Chem. Ed.*, **38**, 590 (1961).

(12) J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

SECONDARY STRUCTURE AND AGGREGATION IN DEOXYGUANOSINE OLIGONUCLEOTIDES

Sir:

Recently the synthesis of deoxyguanosine oligonucleotides bearing 5′-phosphomonoester end groups has been accomplished in this laboratory.[1] Several properties, for example, resistance to venom phosphodiesterase, pointed to secondary structure in these compounds. This communication summarizes results of further studies which show that these oligonucleotides are capable of forming aggregates containing highly ordered polymeric structures. Examination of corresponding oligonucleotides of other deoxyribonucleosides[2] (thymidine, deoxyadenosine, deoxycytidine) under comparable conditions so far has failed to reveal this property in them.

Figure 1 shows the ultraviolet absorption increases in *d*-pGpGpG as a function of temperature. Thus, in 0.25 *M* phosphate buffer (Curve 1) the structure derived from this trinucleotide displays a T_m of about 58°. On keeping the heated solution at room temperature for two weeks the original structure is partially regained (Curve 2). In succinate buffer (0.25 *M*) the behavior is again typical of the collapse of an ordered structure but the T_m is much lower (28°) for an as yet unknown reason. Denaturation of the aggregate also may be accomplished by brief treatment with sodium hydroxide (0.1 *M*) at room temperature. The resulting solution on being kept in 0.25 *M* phosphate buffer for two weeks again displays a T_m of

(1) R. K. Ralph, W. J. Connors, H. Schaller and H. G. Khorana, paper in preparation.

(2) H. G. Khorana and J. P. Vizsolyi, *J. Am. Chem. Soc.*, **83**, 675 (1961); H. G. Khorana, A. F. Turner and J. P. Vizsolyi, *ibid.*, **83**, 686 (1961); R. K. Ralph and H. G. Khorana, *ibid.*, **83**, 2926 (1961).

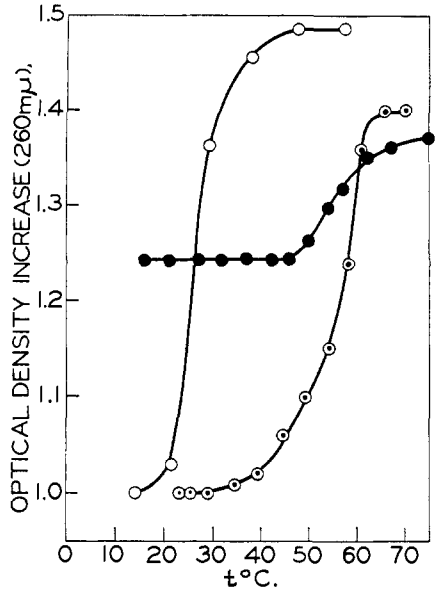

Fig. 1.—Optical density (260 mμ) increases as a function of temperature with *d*-pGpGpG: Curve 1 (-⊙-⊙-), 0.25 *M* phosphate buffer, pH 6.8; Curve 2 (-●-●-) recycling of the solution from Curve 1 after two weeks at room temperature; Curve 3 (-O-O-) melting of a sample (0.01 ml.) of the stock solution of the trinucleotide in 0.25 *M* phosphate buffer (100 optical density units/ml. at 260 mμ) after dilution to 2 ml. in 0.25 *M* succinate–hydrochloride buffer (*p*H 6.55). All readings were taken in cells with 1-cm. light path.

58°. The melting apparently corresponds to reversion to the "monomeric" trinucleotide form. Behavior in the ultracentrifuge (Spinco Model E, ultraviolet optics) further supports the above conclusions. The sample of trinucleotide with T_m of 58° has in the same buffer S_{20} 10–12 whereas after denaturation with alkali and dissolution in the same buffer, its behavior is as expected for the "monomeric" trinucleotide (S_{20} <0.5). The denatured sample on storage at room temperature yields again a high molecular weight aggregate (S_{20} 12–16).

The optical density changes occurring on heating the tetranucleotide (*d*-pGpGpGpG) aggregate are shown in Fig. 2. In 0.25 *M* phosphate buffer complete denaturation was not realized up to 95° (Curve 1). In the 0.25 *M* succinate buffer (Curve 2) and in sodium chloride (0.2 *M*)–phosphate buffer (0.0013 *M*) (Curves 3 and 4) the T_m were much lower. Renaturation to an ordered structure was much faster in the case of the tetranucleotide than with the trinucleotide. Curve 4 shows the recycling of the solution of Curve 3 after keeping at 4° for about two days.

Although detailed studies of other homologs of the above compounds remain to be done, evidence for aggregate formation in the pentanucleotide (*d*-pGpGpGpGpG)[3] was obtained by sedimentation studies (S_{20} 8–10).

(3) The same sample when centrifuged in cesium sulfate equilibrium gradient bands at the buoyant density similar to that observed for ribosomal RNA under the same conditions. We are grateful to Dr. W. Szybalsky for this experiment.

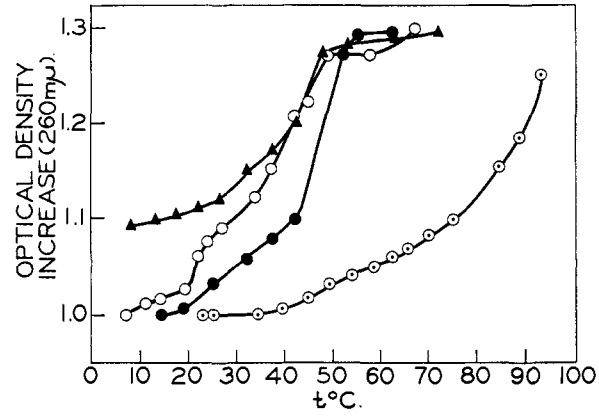

Fig. 2.—Optical density (260 mμ) increases as a function of temperature with the tetranucleotide, *d*-pGpGpGpG: Curve 1 (-⊙-⊙-) in 0.25 *M* phosphate buffer, pH 6.8; Curve 2 (-●-●-) in 0.25 *M* succinate buffer, pH 6.55; Curve 3 (-O-O-) in 0.0013 *M* phosphate + 0.2 *M* sodium chloride; Curve 4 (-▲-▲-) recycling of the solution of Curve 3 after two days at 4°. All readings were taken in cells with 1-cm. light path.

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SAXITOXIN, THE PARALYTIC SHELLFISH POISON. DEGRADATION TO A PYRROLOPYRIMIDINE

Sir:

Saxitoxin, the paralytic poison isolated from toxic Alaska butter clams (*Saxidomus giganteus*), toxic mussels (*Mytilus californianus*), and the plankton *Gonyaulaux catenella*, is among the most toxic known substances. Its pharmacology[1] and biochemistry[2] have been summarized recently. Also, its isolation and purification[3,4] and some of its chemical and physical properties[5] have been described. The molecular formula $C_{10}H_{17}N_7O_4 \cdot 2HCl$ was clearly established[3,4] for saxitoxin, and its most significant degradation product was guanidinopropionic acid, obtained[5] by drastic oxidation with periodic acid or potassium permanganate.

We now wish to report[6] the degradation of saxitoxin to a pyrrolopyrimidine containing eight of the

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(6) Our efforts were generously supported by the U. S. Army Chemical Corps.