light on the effect of solvent on this reaction scheme (Table I).

TABLE I[a]

Compound	Solvent	Atom % excess O^{18} Found		Calculated No equil.	Calculated Equil.
Benzoic Anhydride		1.32	1.30		
Benzanilide	ether	0.44	0.43	0.66	0.44
Benzoic Acid	ether	.87	.88	.66	.88
Benzanilide	water/acetone 2 1	.61	.60	.66	.44
Benzoic Acid	water/acetone 2 1	.70	.70	.66	.88
Benzamide	ammonia	.66	.65	.66	.44
Benzoic Acid	ammonia	.66	.65	.66	.88

[a] Analyzed by the method of W. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953).

When benzoic anhydride labeled in one carbonyl with oxygen-18 is treated with liquid ammonia, benzamide and benzoic acid each containing 50% of the original label are obtained. These results show that the carbonyl oxygen of the amide was a carbonyl oxygen in the anhydride; therefore decomposition of II to products is much faster than return to starting materials. Such a result is not unexpected as ammonia, the solvent, can react with the cation of II to give products. The same anhydride reacts with aniline in ether to give benzanilide containing 33% of the label and benzoic acid containing 67%, a result which can only arise if all of the oxygens in the anhydride become equivalent during the reaction. In this case reversion to starting materials from II could lead to equilibration of the oxygens. Such a process seems reasonable as the most effective base for completing the reaction is benzoate ion. The mode of decomposition of II will be controlled by the nucleophilicity of the benzoate ion as compared to its base strength. In this case, then, return, *i.e.*, nucleophilic displacement, is faster than proton transfer. Such an observation is in accord with the known properties of carboxylate ions, their nucleophilic properties being disproportionately greater than their base strength.[4] Equilibration of the anhydride oxygens could have taken place by reaction with ether to form the oxonium salt. A control experiment in which the anhydride was first treated with ether, reisolated, and then converted to benzanilide in water/acetone (2:1) showed that no equilibration occurred in ether. When the original anhydride was treated with aniline in water/acetone, a small amount of equilibration took place. Return from II, or attack by benzoic acid formed during the reaction on unreacted benzoic anhydride could equally well account for this equilibration. The equilibration found in the ether experiments could possibly have arisen by attack of initially formed benzoic acid on unreacted benzoic anhydride. This reaction would have to be much faster than the conversion to benzanilide. When molar quantities of benzoic anhydride, aniline, radioactive benzoic acid and dimethylaniline (added to promote ionization of the acid) were allowed to react in ether, the benzanilide obtained contained 15% of the radioactivity calculated for complete exchange of all benzoyl containing species.[5] Since the concentration of benzoic acid was much greater in this experiment than in the oxygen-18 equilibration studies, only a very small amount of the oxygen equilibration can arise through an intermolecular reaction involving benzoic acid. The carbon-14 exchange found could have either occurred by attack on benzoic anhydride, II or both. A control experiment without aniline showed that benzoic anhydride undergoes a slow exchange with radioactive benzoic acid under these conditions. Further work on these reactions is now in progress; particular attention is being devoted to the nature and properties of II in various solvents.

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[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, pp. 451.

[5] We wish to thank Dr. A. P. Wolf of the Brookhaven National Laboratory for his aid in carrying out these experiments.

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STRUCTURE OF DITHIONITE

Sir:

The structure of the dithionite anion has been established by X-ray analysis of crystals of anhydrous sodium dithionite (hydrosulfide, hydrosulfite), $Na_2S_2O_4$. The crystals are monoclinic, $a = 6.404 \pm 0.0045$ Å., $b = 6.559 \pm 0.0028$ Å., $c = 6.586 \pm 0.0045$ Å., $\beta = 119°31' \pm 0° 02'$, space group P2/c, with four formula units of $NaSO_2$ in the unit cell. The space-group conditions require the doubled unit, $Na_2S_2O_4$, to possess either a center of symmetry or a two-fold rotation axis parallel to *b*.

The details of the structure have been determined and refined by repeated $F_0 - F_c$ Fourier projections[1] down the three axes which led eventually to disagreement factors $R = \Sigma|F_0 - F_c|/\Sigma|F_0|$ of 0.098, 0.063 and 0.106 for (*hk*0), (*h*0*l*), and (0*kl*) reflections, respectively. The final atomic positions have estimated standard deviations of 0.008 Å. for sulfur, 0.011 Å. for sodium and 0.015 Å. for oxygen. The anion has approximate C_{2v} symmetry, the two independent S–O distances (1.496 Å. and 1.515 Å.) and O–S–S angles (98°01′ and 99°23′) not differing significantly. The S–S distance, 2.389 Å., is much longer than that in a typical disulfide bond, 2.08 Å.[2]. Pauling's relationship between covalent radius and bond number, $-\Delta R(n) = 0.353 \log n^3$, leads to a bond number *n* of 0.36.

The dithionite anion can thus be regarded as a pair of SO_2^- units linked by a weak S–S bond. Although the existence of the free radical anion SO_2^- has not been demonstrated directly, the rapid exchange of S^{35} between dithionite and sulfur

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[1] W. Cochran, *Acta Cryst.*, **4**, 81, 408 (1951).

[2] S. C. Abrahams, *ibid.*, **7**, 423 (1954).

[3] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

dioxide[4] would indicate that it must occur at least as a transitory species. One might expect, moreover, a marginal stability for the monomer since the isoelectronic molecule chlorine dioxide does not dimerize to an appreciable extent. The reducing action of dithionite can now be pictured as proceeding simply by loss of an electron to any suitable acceptor with formation of sulfur dioxide.

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[4] H. B. van der Heijde, *Rec. trav. chim.*, **72**, 95 (1953).

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NON-AQUEOUS SOLUTIONS OF SODIUM DESOXYRIBOSE-NUCLEATE

Sir:

Present hypotheses[1] concerning the structure of sodium desoxyribose nucleate (DNA) are based entirely on experiments with the hydrated polymer. Consequently, the extent to which water itself participates in stabilizing the structure has remained uncertain or ignored. We have discovered that it is possible to prepare solutions of DNA in a number of organic solvents[2] by dialysis and this communication concerns the novel properties of DNA in absolute ethanol.

Two different samples of calf thymus DNA, samples A and SB11B, prepared according to the method of Simmons[3] were used.[4] Dialysis of pure water solutions of DNA against increasing concentrations of ethanol yielded stable absolute ethanol solutions whose light scattering and sedimentation behavior indicates a drastic change of configuration at constant molecular weight. The comparison of macromolecular properties of sample SB11B in ethanol and 0.2 M NaCl in water (Table I) deserves further comment. The measured molecular weights in 0.2 M NaCl and ethanol differ by 15%. This is within the limits of experimental error.[7] On the other hand, the change in the radius of gyration is tremendous, especially when it is recalled that DNA is more extended in pure water than in 0.2 M NaCl.[8] As a consequence of this molecular collapse, ethanol solutions of DNA demonstrate little concentration dependence of the sedimentation constant and no hypersharpening of the sedimentation boundary. In addition, the intrinsic viscosity undergoes a fiftyfold decrease.

TABLE I

PROPERTIES OF CALF THYMUS DNA (SAMPLE SB11B)

	0.2 M NaCl[a]	100% Ethanol
Molecular weight[b]	7.7×10^6	6.6×10^6
Radius of gyration, A^b	3000	980
Sedimentation constant, $[S_{20,w}]_{c=0}$	21	65

[a] From reference (5). [b] From light scattering. For discussion of the averages determined for these quantities by the double extrapolation of reciprocal scattering to zero angle and concentration, see reference (6).

Two additional experiments are of interest: the first (Fig. 1) follows the change of sedimentation constant of sample SB11B in ethanol–water mixtures of varying composition. The change of DNA configuration is shown to occur rather sharply at about 65% ethanol content. It is not accompanied by the increase in ultraviolet absorption associated with denaturation.[9] The second experiment shows that the ethanol configuration change is essentially reversible with respect to size and shape. The light scattering of sample A in .2 M NaCl before and after dialysis[10] against 100% ethanol was compared. Molecular weights of 5.2 and 4.9 million, radii of gyration of 2060 and 1830 Å. and $s_{20,w}$ in 0.03% solution of 11.5 and 13.1, respectively, were obtained. While the redialyzed DNA is not as highly extended as the native material, a very closely similar structure has been reformed. This contrasts sharply with the irreversible change of shape produced by heating aqueous solutions.[5,11] It would be of interest to establish whether the ethanol configuration change is also reversible with respect to biological activity.

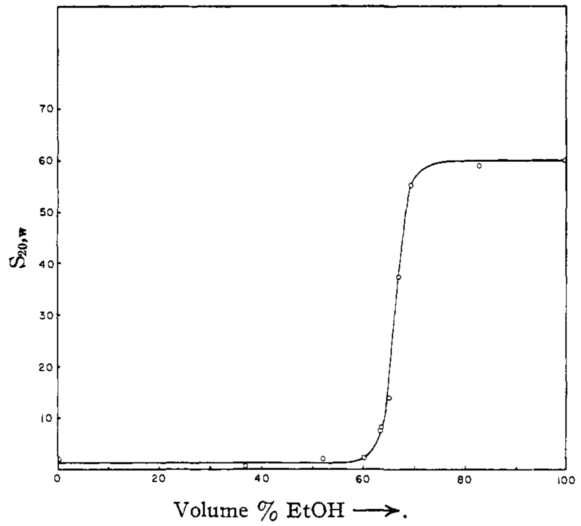

Fig. 1.—Sedimentation constant of DNA, sample SB11B, in ethanol–water mixtures as a function of solvent composition. The solute concentration varies between 0.06 and 0.13%.

Further evidence[5] against the interrupted chain

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[1] F. H. C. Crick and J. D. Watson, *Proc. Roy. Soc.*, **A223**, 80 (1954).

[2] The solubilities of a large number of proteins and DNA in organic solvents have also been investigated by E. D. Rees and S. J. Singer, *Arch. Biochem. Biophys.*, in press.

[3] N. Simmons, Atomic Energy Commission Report UCLA 184.

[4] Sample SB11B was the generous gift of Professor Paul Doty, which we gratefully acknowledge. It had been prepared by Dr. Simmons according to his method.

[5] P. Doty and S. Rice, *Biochim. Biophys. Acta*, **16**, 447 (1955).

[6] H. Benoit, *J. Polymer Sci.*, **11**, 507 (1953).

[7] Not only must the uncertainty of the double extrapolation to zero angle and concentration be considered, (especially in ethanol), but in addition the two measurements were made on different instruments, introducing the absolute calibrations as a source of divergence.

[8] J. W. Rowen, *Biochem. Biophys. Acta*, **10**, 391 (1953).

[9] R. Thomas, *ibid.*, **14**, 231 (1954).

[10] The dialyzed sample was submitted to the following series of steps: exhaustive dialysis against water was followed by dialysis against increasing concentrations of ethanol, redialysis against increasing concentrations of water, and a final dialysis of this aqueous solution against 0.2 M NaCl.

[11] S. Zamenhof, H. Alexander and G. Leidy, *J. Exptl. Med.*, **98**, 373 (1954).