relation with σ^+ infers a direct resonance interaction of the substituent with the incipient benzyl radical, influencing to some extent resonance structure I of the proposed transition state for electron transfer.[16-19]

$$[ArCH_2CO_2^-SO_4\cdot^- \longleftrightarrow \underset{I}{ArCH_2^+CO_2\cdot{}^-SO_4^{2-}} \longleftrightarrow ArCH_2CO_2\cdot SO_4^{2-}]$$

As yet incomplete results from our laboratory on alkyl-, diaryl-, and triaryl-substituted acetic acids indicate a duality of mechanism, or a continuum for the degree of bond breaking during the electron-transfer process, which seems to correlate with the stability of the radical (R·) formed. The results of this work will be reported at a later date.

Acknowledgment. We are indebted to the National Research Council of Canada and the University of Alberta for their generous support of this work.

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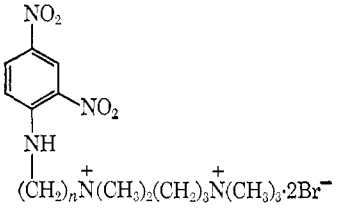
Topography of Nucleic Acid Helices in Solutions. XI. A Novel Method of Distinguishing between Ribo- and Deoxyribonucleic Acids by the Use of Reporter Molecules[1]

Sir:

We report the results of a preliminary study of the effect of double-stranded native and denatured ribo- and deoxyribonucleic acid helices on the uv and induced CD of the reporter molecules **1** and **2**. In line with our previous report on single- and double-stranded homo-



1, $n = 2$
2, $n = 3$

polymers,[1] substantial hypochromism in the near-uv absorption spectrum and an induced CD of the reporter molecules are observed on binding to nucleic acids. The effect of various polynucleotide systems on the absorption spectra of **1** and **2** is summarized in Table I. Several interesting points may be made. (1) The transition in the 350-mμ region is probably a charge-transfer $\pi^* \leftarrow \pi$ type since it has an extinction coefficient, ϵ_{max}, of 16,000, characteristic of an allowed transition, and a red shift in the maximum is observed in going from 95% ethanol to 0.01 *M* sodium phosphate buffer (338 → 350 mμ and 343 → 356 mμ for $n = 2$ and 3, respectively).[1,2] (2) Interaction of the reporter molecule with all the nucleic acids studied leads to a complex in which the environment of the chromophore is more polar than that of water since a further shift to the red is observed (350 → 355 mμ and 356 → 362 mμ for $n = 2$ and 3, respectively). (3) Substantial hypochromism is observed when the reporter molecule is bound to the polynucleotides. The extent of hypochromism appears to depend on the nucleic acid system and not on the number of methylene groups, *n*, between the ring nitrogen and quaternary nitrogen of the reporter molecule. The per cent hypochromicity of the reporter molecule is greater upon binding deoxyribonucleic as compared with ribonucleic acid (Table I). Moreover, there is a slight decrease in the hypochromism of **1** and **2** upon denaturing the nucleic acid (at least in the case of DNA).

Table I. The Effect of Ribo- and Deoxyribonucleic Acids on the Absorption Spectra of Reporter Molecules **1** and **2**[a]

	Reporter molecule							
	1, $n = 2$				**2**, $n = 3$			
Conditions	λ_{max}, mμ	ϵ_{max}	% H[b]	P/R[c]	λ_{max}, mμ	ϵ_{max}	% H[b]	P/R[c]
95% EtOH	338	16,600			343	16,050		
H_2O-buffer[d]	350	16,600			356	16,160		
Salmon testes								
DNA (N)[e]	355	10,060	65	80	362	10,340	56	80
DNA (D)[f]	355	10,780	53	80	361	10,300	57	80
Calf thymus								
DNA (N)[e]	355	10,000	66	74	362	9,680	67	74
DNA (D)[f]	355	10,860	52	74	361	10,660	52	74
Yeast								
RNA (N)[e]	354	12,300	35	80	361	11,100	46	80
RNA (D)[f]	355	11,860	40	80	361	11,295	43	80
Torula								
RNA (N)[e]	355	11,800	41	80	361	12,330	31	80
RNA (D)[f]	355	12,130	36	80	361	11,800	37	80

[a] At 25.0 ± 0.2° in 0.01 *M* sodium phosphate buffer, pH 6.40–6.50 (0.01 *M* in Na^+). All uv spectra were taken in 10-mm cells using a Cary 14 spectrometer at 25.0 ± 0.2°. Values of λ_{max} and ϵ_{max} in the presence of nucleic acid reported in this table are limiting values, *i.e.*, additional change in spectra is not observed at further excess of nucleic acid. [b] % hypochromicity (% H) = $[\epsilon_{max}(H_2O)/\epsilon_{max}(p) - 1.0]100$, where $\epsilon_{max}(H_2O)$ and $\epsilon_{max}(p)$ are the extinction coefficients in the absence and presence of the polynucleotides. [c] P/R indicates the ratio polynucleotide phosphate/reporter molecule. In all cases reported above, 5×10^{-5} *M* **1** or **2** was used. [d] In 0.01 *M* sodium phosphate buffer (0.01 *M* in Na^+), pH 6.50. [e] Native (N) calf thymus and salmon testes DNA are Worthington products Lot No. 642 and 6CFA, respectively. Yeast RNA (Lot 6234) and torula RNA (Lot 55711) were obtained from Worthington and Calbiochem, respectively. [f] Denatured (D) nucleic acids were obtained by heating in a boiling water bath for 15 min and then immediate quenching in ice water.

The dramatic effect, however, arises from the induced circular dichroism of **1** and **2** upon binding to RNA and DNA. Figure 1 shows the CD results of **1** and **2** bound to native calf thymus and salmon testes DNA and to yeast and torula RNA. A summary of the results including the molar ellipticities, [θ], of the (positive) peaks and (negative) troughs together with the associated wavelengths for the complexes formed with native and denatured DNA and RNA are shown in Table II.

(1) Part X: E. J. Gabbay and J. Mitschele, submitted for publication.
(2) The large red shifts observed on changing solvents (95% EtOH to H_2O) which correspond to 2.9 and 3.0 kcal for **1** and **2**, respectively, are indicative of an intramolecular charge-transfer transition: J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," John Wiley & Sons, Inc., New York, N. Y., 1963, p 305.

Table II. Effect of Various Nucleic Acids on the Induced CD Spectra of Reporter Molecules **1** and **2**[a]

Polynucleotide	**1**, $n = 2$					**2**, $n = 3$				
	λ, mμ	$[\theta] \times 10^{-3}$, deg	λ, mμ	$[\theta] \times 10^{-3}$, deg	P/R[b]	λ, mμ	$[\theta] \times 10^{-3}$, deg	λ, mμ	$[\theta] \times 10^{-3}$, deg	P/R[b]
Calf Thymus										
DNA (N)			360	−9.40	22			365	−6.73	22
DNA (D)[c]			357	−1.45	22			365	−2.76	22
DNA (D)[d]			357	−3.12	22					
Salmon Testes										
DNA (N)			360	−9.60	24			365	−6.24	24
DNA (D)[c]			360	−3.48	24			370	−2.41	24
DNA (D)[d]			360	−4.08	24					
Yeast										
RNA (N)	357	7.80			24	360	8.68			24
RNA (D)[c]	355	7.74			24	361	8.93			24
Torula										
RNA (N)	358	7.44			24	360	7.44			24
RNA (D)[c]	357	7.62			24	360	7.23			24

[a] CD curves were measured in a Cary 60 recording spectropolarimeter equipped with a Model 6001 CD accessory at 26.0 ± 0.4° in 10-mm cells. The solution contained 1.67×10^{-4} *M* **1** or **2** in 0.01 *M* sodium phosphate buffer (0.01 *M* in sodium), pH 6.40–6.50. [b] The ratio of moles of polynucleotide phosphorus to moles of reporter molecules in solution. [c] Denatured nucleic acid (see footnote *f* of Table I). [d] Denatured DNA after standing at room temperature for 26 hr.

Several interesting points may be made. (1) RNA and DNA induce opposite CD behavior in the absorption band of the reporter molecules **1** and **2**.[3] Ribose-containing nucleic acids induce a positive Cotton effect similar to what has been found for the double-stranded homopolymers, *i.e.*, polyriboadenylic–polyribouridylic and polyribocytidylic–polyriboinosinic acid helices.[1] (2) A dependence of the observed molar ellipticity on the P/R (moles of polynucleotide phosphorus/mole of reporter molecules) ratio was found; as $P/R \rightarrow 0$, $[\theta] \rightarrow 0$; as $P/R \rightarrow \infty$ ($P/R \approx 24$ was the largest ratio studied), $[\theta]$ approaches a limiting value. (3) The molar ellipiticity of the DNA reporter complex depends on n, *i.e.*, it is larger for $n = 2$ than for $n = 3$. On the other hand, the molar ellipiticity of the RNA reporter complex is relatively unchanged for native torula RNA and is smaller for $n = 2$ than for $n = 3$ for yeast RNA (Table II). (4) Denatured DNA induces a lower CD effect in the absorption band of **1** and **2** than native DNA. The results are consistent with the idea that the induced CD spectrum depends on the interaction with double-stranded helical rather than the single-stranded random-coil regions of DNA. On allowing the denatured DNA to anneal (26 hr at room temperature) the molar ellipticity increases slightly in line with the above interpretation. (5) Native and denatured RNA complexes with **1** and **2** show approximately the same molar ellipticities. The results are not surprising since the commercial preparation of yeast RNA and torula RNA involve a similar denaturation step.

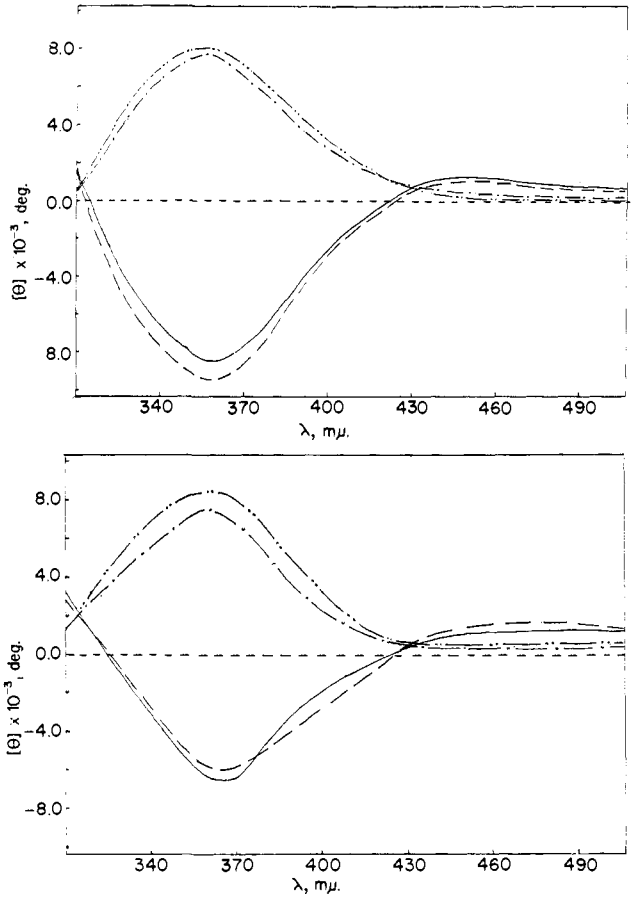


Figure 1. CD spectra of reporter molecules **1** and **2** in the presence of nucleic acid: (a) (top) reporter **1** in the presence of yeast RNA (— · · —), torula RNA (— · —), calf thymus DNA (———), and salmon testes DNA (— — —); (b) (bottom) same as in a but using reporter **2** (see Table II).

In summary, subtle differences in the topography of the surface of nucleic acids systems are amenable to investigation by the use of reporter molecules. Further work along this area is in progress.

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(3) The origin of the oppositely induced CD is not totally clear. However, work in progress strongly suggests that it involves the orientation of the ring chromophore of **1** or **2** with respect to the helix axis (E. Gabbay, 1968).

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