The close correlation of spectra of I and II with VI and VII further substantiates the assignment of I and II as phenonium ions. The methoxy group is more deshielded in VI than in I because, in the latter, charge is delocalized also into the cyclopropane ring. This may also explain that even at -70° in I rotation of the methoxy group is relatively free (less C–O double bond character than in ion VI), and the *ortho* ring protons are equivalent.

The AB quartets are well separated, indicating the benzenonium ion character of the ions and substantial differences in the shieldings of A and B. (This excludes Brown's suggested rapidly equilibrating π-bridged ions,[5b] because these should have phenyl, but not benzenonium character.) Further, the cyclopropyl protons in spiro[2.5]octa-1,4-dien-3-one were found by Baird and Winstein[10] as a sharp singlet. Eberson and Winstein observed the cyclopropyl protons in the bridged anthryethyl ion at -3.44 ppm.[3] Comparing these data with those of the *p*-anisonium ion I provides a strong case of direct analogy and further strengthens the assignment of I as a bridged phenonium ion.

All spectra (if otherwise not shown) were obtained at -60° with external TMS as reference (sealed capillary tube). Acid peaks have been deleted, to simplify spectra.

From all data, we must conclude that we observed in SbF_5–SO_2 solution of β-*p*-anisylethyl and β-mesitylethyl chloride at -60° the bridged *p*-anisonium and 2,4,6-trimethylphenonium ions, the first phenonium ion to be observed formed by direct aryl participation.

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(11) National Science Foundation Postdoctoral Research Investigator, 1965–1966.

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Hindered Rotation around the S–S Bond in the Anomeric Di-5-(2′-deoxyuridilyl) Disulfides[1]

Sir:

We recently reported the synthesis of the anomeric 5-mercapto-2′-deoxyuridines.[2] These compounds readily undergo autoxidation[3] to the corresponding disulfides, I(α) and II(β). We found that the latter compounds show surprisingly large optical rotations compared to the original thiols or to their S-methyl derivatives,[4] III(α) and IV(β), respectively (see Figure 1).

The high optical rotatory power of cystine was noted by van't Hoff. Fieser[5] explained this apparent anomaly with the proposed formation of a system of three ten-membered rings with stable hydrogen bonds, while Fredga[6] attributed it to the proximity of the S–S bond to an asymmetric carbon atom. The latter view was also expressed by Balenovic, *et al.*,[7] who found that β-homocystine had a much higher specific rotation than homocystine; in the latter, the S–S bond is removed from the asymmetric carbon by one more methylene group. However, neither of these explanations seems to be satisfactory in the case of the title compounds in which the S–S bond is removed from the nearest asymmetric center of the molecule by three atoms of the pyrimidine ring.

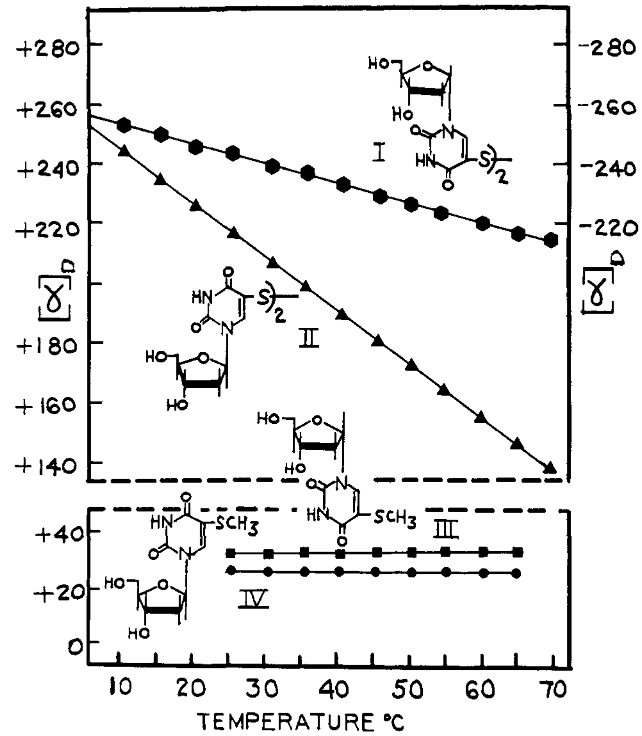

Figure 1. Temperature dependence of optical rotations: ●-●-●, compound I, negative $[\alpha]_D$ values (ordinate, scale at the right); ▲-▲-▲, compound II, positive $[\alpha]_D$ values (ordinate, scale at the left); ■-■-■ compound III, and ●-●-●, compound IV, low positive $[\alpha]_D$ values (ordinate, scale at the left).

More recently, Strem, *et al.*,[8] studied the optical rotatory dispersion of amino acids and suggested that the unusually large rotation and Cotton effect of cystine may be due to the asymmetric configuration of the S–S bond.[9] It has been suggested,[10] and demonstrated in the case of a number of disulfides,[11] that the valencies of two bonded sulfur atoms form a dihedral angle of about 90–100° (between the two S–S–C planes), resulting in two symmetrical energy minima for rotations around an S–S linkage.[12] The rotational barrier has been calculated for a few simple disulfides from spec-

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Table I. Structural Features of Some Disulfides

Compound	ϕ_{SS},[a] deg	S–S, A	C–S, A	∠CSS, deg
L-Cystine[b]	74	2.032 (±0.004)	1.82 (±0.01)	104.5 (±0.5)
CH_3S–SCH_3[c]	85	2.038	1.810	102.8
N,N^{1}-Diglycyl-L-cystine[d]	89	2.04 (±0.005)	1.87 (±0.02)	103 (±1)
CF_3S–SCF_3[e]	*e*	2.05 (±0.02)	1.83 (±0.02)	105 (±3)
I	49	2.108 (±0.003)	1.763	101.4
			1.749 (±0.007)	102.3 (±0.2)

[a] The standard deviation of this torsional angle for the various compounds approximately ranges between 1 and 2°. [b] B. M. Oughton and P. M. Harrison, *Acta Cryst.*, **12**, 396 (1959). [c] D. Sutter, H. Dreizler, and H. O. Rudolph, *Z. Naturforsch.*, **20**, 1676 (1965). [d] H. L. Yakel and E. W. Hughes, *Acta Cryst.*, **7**, 291 (1954). [e] H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954), assumed ϕ_{SS} to be about 90°.

troscopic measurements to be between 9.5 and 14.2 kcal/mole.[13] Therefore, it seemed to us that the large increase in the optical rotatory power of the disulfides I and II in comparison to the corresponding thiols may be due to hindered rotation around the S–S bond.

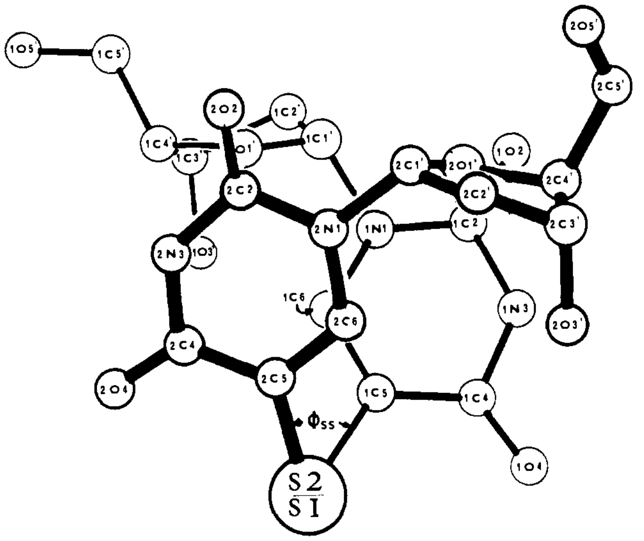

Figure 2. Projection of molecular structure of I down the disulfide bond (hydrogen atoms are not shown).

In order to test this hypothesis, we determined the optical rotations of the disulfides I and II, and, for comparison, those of the corresponding methyl sulfides, III and IV, at various temperatures between +1 and 70°. Figure 1 clearly shows the very strong decrease of the optical rotatory power with increasing temperature in the case of the disulfides, in sharp contrast to the relative constancy of the rotation values for the methyl sulfides within the given temperature range. These results are consistent with an interpretation that the "excess" optical rotatory power of the disulfides results from the particular spatial arrangement of the 2'-deoxyuridyl groups around the S–S bond in the most stable conformation of the molecule. Elevation of the temperature helps to overcome the rotational barriers and tends to equalize the different conformations. It is apparent from Figure 1 that the optical rotation of II changes (in opposite direction) about twice as fast with temperature than that of I, and that at low temperatures the two anomers have nearly equal and opposite rotations. This suggests the possibility that the S–S bonds may have opposite chiralities in the preferred conformations of the two anomers.

The molecular structure of I was determined by X-ray diffraction in an effort to gain further insight into the structural factors behind the hindered rotation about the disulfide bond. In Table I, the essential features of the disulfide linkage of I are compared with those of some other accurately determined open-chain disulfides. The electronic state of I is quite profoundly different from the other compounds of the tabulation. The azimuthal angle (ϕ_{SS}, defined as the projected C–S–S–C angle) does not agree with the position of a theoretical energy minimum (at 90°) for the rotation around an S–S bond if the rotational barrier is solely attributed to an overlap of the unshared p electrons.[10,11] The large degree of double bond character in the C–S bonds could increase the electron density in the S d orbitals and thereby cause an overlap of 3d electrons, which may result in repulsion between the two sulfurs and in the lowering of the azimuthal angle. This is in agreement with the significantly longer S–S bond of I. In addition, the resonance of the C–S bonds appears to influence the electronic states of the uracil moieties, where the C_5–C_6 bond lengths were found to be substantially longer (1.353 and 1.368 A (±0.010)) than the average value reported for this bond in other pyrimidine nucleosides and nucleotides (1.33 ± 0.01 A).

The structure of the molecule (Figure 2) in which the two nucleoside groups appear in a nearly staggered conformation indicates that the internal rotation may be influenced by both the base and the sugar. X-Ray structural analysis on other compounds of this series is in progress in order to elucidate this phenomenon in detail.

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