# The Crystal Structure of Disodium 4-Oxypyrimidine-2-sulfinate Hexahydrate

**Jorunn Sletten**[1]

*Contribution from the Department of Biological Structure, University of Washington, Seattle, Washington 98105.*

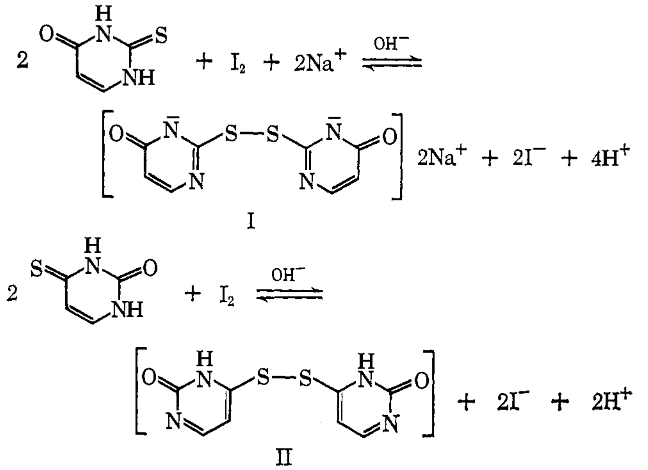
*Received February 12, 1969*

**Abstract:** The crystal structure of disodium 4-oxypyrimidine-2-sulfinate hexahydrate, $Na_2[C_4H_2N_2OSO_2]\cdot 6H_2O$, has been determined by single-crystal X-ray analysis. The crystals are orthorhombic, space group Pbcm, $a$ = 9.2988 (4), $b$ = 20.2529 (8), and $c$ = 6.9460 (8) Å. There are four formula weights per unit cell. The thiouracil moiety is in a crystallographic mirror plane while the two sulfinate oxygens are twisted out of the plane. The C—S and the S—O bonds (1.835 ± 0.003 and 1.516 ± 0.004 Å, respectively) are somewhat longer than corresponding bonds in sulfonates. The C═O bond length of 1.274 ± 0.004 Å is of the same magnitude as the predicted carbon–oxygen bonds in carboxylate ions.

For some time a program of research has been under way in this laboratory to establish accurate dimensions for nucleic acid components and related molecules. Several of these compounds possess chemotherapeutic activities, but the mechanisms involved are, in most cases, still unknown.

2-Thiouracil is known to inhibit the thyroid hormone while 4-thiouracil is inactive.[2] The activity of 2-thiouracil has been considered to depend upon its rapid reaction with iodine. However, this reaction is not the only factor to be considered, since the inactive compounds such as, *e.g.*, 6-amino-2-thiouracil are equally reactive toward iodine.

To shed more light on the electronic difference of the 2 and 4 positions in uracil, it was decided to carry out X-ray crystallographic determinations of the products formed by the reactions of iodine and 2-thiouracil and 4-thiouracil, respectively. Miller, *et al.*,[3] have described the pathway for these reactions, and have isolated and identified the reaction products as the disulfide disodium salt of 2-thiouracil (I) and the free disulfide of 4-thiouracil (II). These disulfides are not very stable; an ionic scission of the sulfur–sulfur bond may take place in alkaline solution,[4] giving sulfinic acid and sulfide through the reaction steps



$$RS \longrightarrow SR + OH^- \longrightarrow RSOH + RS^-$$

$$2RSOH \longrightarrow RSO_2H + RSH$$

In the course of the crystallographic investigation it became evident that a scission of the S—S bond had indeed taken place.

## Experimental Section

White, flaky crystals were obtained from a reaction mixture of iodine and 2-thiouracil in 1 $N$ NaOH by adding acetone.[3] The compound dissolved easily in cold water. Thin, colorless needles were obtained by diffusing acetone into a fairly concentrated solution.

Weissenberg films showed that the crystals are orthorhombic. Reflections are systematically absent for $0kl$ when $k = 2n + 1$ and for $h0l$ when $l = 2n + 1$; accordingly, the space group may either be Pbcm or Pbc2. A Wilson plot which was subsequently calculated for the complete set of data strongly favored the centrosymmetric space group Pbcm.

The unit cell dimensions were derived from the least-squares treatment of the $2\theta$ settings for 12 reflections measured on a four-circle diffractometer using Cu K$\alpha$ radiation ($\lambda$ 1.5418 Å): $a$ = 9.2988 (4), $b$ = 20.2529 (8), and $c$ = 6.9460 (8) Å.

The density, determined by flotation in a mixture of chloroform and tetrabromoethane, was found to be 1.58 ± 0.01 g cm$^{-3}$. The calculated density of the disulfide, $Na_2{}^+[C_8H_4N_4O_2S_2]^{2-}\cdot H_2O$, assuming four formula weights per unit cell, is 1.607 g cm$^{-3}$. The difference between the experimental and theoretical density is within three times the estimated standard deviation. This discrepancy is too small to rule out the possibility of a disulfide structure. The density calculated for the actual structure, which turned out to be the disodium sulfinate of 2-thiouracil, $Na_2{}^+C_4H_2N_2OSO_2]^{2-}\cdot 6H_2O$, is 1.586 g cm$^{-3}$, in good agreement with the density determined experimentally.

The crystal used for collecting data had dimensions 0.52 × 0.12 × 0.03 mm. It was mounted along the needle axis which coincides with the crystallographic $c$ axis. The integrated intensities were measured using the $\theta$-$2\theta$ scan technique and Cu K$\alpha$ radiation. Three standard reflections, measured every 4 hr throughout the data collection, indicated that the crystal was deteriorating, and by the end of the data collection, the standard reflections had suffered an average decrease of 6%. The data collected within each 4-hr interval were scaled by the factor found for the standard reflections. Of a total of 1224 reflections which were collected within a sphere limited at $\sin(\theta/\lambda) = 0.59$, 1084 had intensities significantly greater than their background counts.

The data were corrected in the usual way for Lorentz and polarization effects. After the structure was solved and refined to $R$ = 0.06, an absorption correction was applied using the analytical

---

(1) Address inquiries to the Department of Chemistry, University of Bergen, Bergen, Norway.

(2) E. B. Astwood, A. Bissell, and A. M. Hughes, *Endocrinology*, 37, 456 (1945).

(3) W. H. Miller, R. O. Roblin, Jr., and E. B. Astwood, *J. Am. Chem. Soc.*, 67, 2201 (1945).

(4) O. Foss, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, Symposium Publications Division, New York, N. Y., 1961, p 83.

**Table I.** Final Coordinates and Thermal Parameters for the Nonhydrogen Atoms[a]

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S | 0.56772 (9) | 0.38327 (4) | 0.25000 (0) | 1.79 (3) | 1.83 (3) | 3.77 (5) | −0.13 (3) | 0.00 (0) | 0.00 (0) |
| N(1) | 0.47840 (26) | 0.25688 (13) | 0.25000 (0) | 1.86 (10) | 1.87 (12) | 4.73 (16) | 0.12 (10) | 0.00 (0) | 0.00 (0) |
| N(3) | 0.29646 (26) | 0.34045 (12) | 0.25000 (0) | 1.79 (11) | 1.76 (11) | 3.24 (14) | 0.04 (9) | 0.00 (0) | 0.00 (0) |
| C(2) | 0.43009 (33) | 0.31834 (15) | 0.25000 (0) | 2.04 (13) | 2.08 (13) | 3.05 (16) | −0.08 (11) | 0.00 (0) | 0.00 (0) |
| C(4) | 0.18869 (33) | 0.29427 (15) | 0.25000 (0) | 2.01 (14) | 2.38 (14) | 2.93 (16) | 0.01 (11) | 0.00 (0) | 0.00 (0) |
| C(5) | 0.22943 (35) | 0.22673 (16) | 0.25000 (0) | 2.07 (13) | 2.12 (14) | 4.00 (19) | −0.20 (11) | 0.00 (0) | 0.00 (0) |
| C(6) | 0.37072 (37) | 0.21120 (17) | 0.25000 (0) | 2.65 (15) | 1.96 (15) | 4.57 (21) | 0.25 (12) | 0.00 (0) | 0.00 (0) |
| Na(1) | 0.31327 (13) | 0.75000 (0) | 0.50000 (0) | 2.37 (5) | 2.88 (6) | 3.68 (7) | 0.00 (0) | 0.00 (0) | 0.29 (6) |
| Na(2) | −0.01430 (15) | 0.51537 (7) | 0.25000 (0) | 3.00 (6) | 3.08 (7) | 4.50 (8) | −0.07 (5) | 0.00 (0) | 0.00 (0) |
| O(2) | 0.65357 (17) | 0.36417 (8) | 0.42698 (27) | 2.80 (7) | 2.93 (7) | 3.89 (9) | −0.51 (6) | −0.76 (7) | 0.03 (7) |
| O(4) | 0.05849 (22) | 0.31386 (11) | 0.25000 (0) | 1.49 (9) | 2.46 (10) | 5.40 (15) | 0.14 (8) | 0.00 (0) | 0.00 (0) |
| O(7) | 0.05836 (23) | 0.58619 (11) | 0.50845 (36) | 2.81 (8) | 5.03 (11) | 5.86 (13) | −0.07 (8) | 0.05 (10) | −2.37 (10) |
| O(8) | 0.21694 (37) | 0.47310 (17) | 0.25000 (0) | 2.98 (15) | 2.12 (13) | 15.71 (39) | 0.29 (12) | 0.00 (0) | 0.00 (0) |
| O(9) | −0.24999 (46) | 0.53648 (28) | 0.31339 (90) | 2.65 (21) | 7.67 (28) | 7.19 (46) | 0.76 (20) | −0.01 (21) | 0.05 (21) |
| O(10) | 0.15157 (29) | 0.72301 (17) | 0.25000 (0) | 2.16 (11) | 2.82 (13) | 5.03 (16) | 0.16 (11) | 0.00 (0) | 0.00 (0) |
| O(11) | 0.43835 (32) | 0.56402 (14) | 0.25000 (0) | 4.02 (14) | 3.31 (13) | 4.70 (17) | −0.52 (11) | 0.00 (0) | 0.00 (0) |

[a] The thermal parameters are defined by: $T_i = \exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

method described by Meulenaer and Tompa.[5] The linear absorption coefficient for the sulfinate (Cu K$\alpha$ radiation) is 32.2 cm$^{-1}$, and the transmission coefficients calculated by the program were in the range 0.70–0.99. The total error assigned to the net intensity of each reflection is $\sigma_I = [N_T + (0.01N_T)^2]^{1/2}$, where $N_T$ is the total count of backgrounds and scan. The standard deviation in the structure factors was estimated at $\sigma_F = [F^2 + \sigma_I(\mathrm{Lp})^{-1}]^{1/2} - F$.

## Structure Determination

At the outset it was not clear whether the structure was a disulfide, a sulfide, or a sulfinate. A sharpened origin removed Patterson map did not give any sulfur–sulfur vector of appropriate length for a disulfide bond. Only one sulfur atom, lying in a crystallographic mirror plane, could be located. A Fourier synthesis based on phases determined by this atom ($R = 0.645$) did not reveal the uracil ring. An attempt was then made to solve the structure by symbolic addition using the SIGMA 2 and PHASE programs from the X-ray 67 system.[6] The solution arrived at had no inconsistencies, and the $E$ map based on 130 terms ($E > 1.5$) showed one complete thiouracil molecule with all the atoms lying in the mirror plane. In addition, there were several other peaks of electron density, two of which were definitely more prominent than the others.

The position of the sulfur atom in the $E$ map agreed with the position derived from the Patterson map. Two peaks, related by a mirror plane and located approximately 1.5 Å from the sulfur atom, could be interpreted as part of a sulfinate group. However, these peaks were much smaller than the one representing the carbonyl oxygen in the 2-thiouracil moiety. Therefore they were not included in the initial Fourier synthesis. A structure factor calculation based only on the atoms in the thiouracil molecule gave an $R$ of 0.585 ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). At this stage only one sodium ion was expected to be present in the structure. Both the $E$ map and the Patterson map indicated that this ion was located on a twofold axis, and although the preceding Fourier map did not support this assumption, the Na$^+$ ion was included in the following structure factor calculation. $R$ decreased to 0.52, and several well-formed peaks could now be distinguished in the Fourier map. Five of these sites were tentatively assigned oxygen atoms reducing $R$ to 0.38. A least-squares cycle did not improve the $R$ factor. However, a large negative shift in the thermal parameter for one of the oxygen atoms and evidence from the Patterson and the $E$ map suggested that the site was, in fact, occupied by a sodium ion. At this stage the oxygen atom in the sulfinate group was also included in the refinement. One least-squares cycle with isotropic thermal parameters followed by another cycle with anisotropic thermal parameters lowered $R$ to 0.078. The function minimized in the full-matrix least-squares refinement was $\Sigma w(F_o - F_c)^2$, where $w = 1/\sigma_F$.

A difference map gave the positions of all hydrogen atoms except those on water oxygen O(9) (Figure 1). This oxygen atom, located in the mirror plane, had refined to an unreasonably high $B_{33}$ value (25 Å$^2$), indicating that the atom might be disordered. To improve the model for the least-squares refinement, the atom was split in two halves tentatively placed 1 Å apart. The half oxygen atom refined well and settled at a distance of 0.4 Å from the mirror plane. The hydrogen atoms attached to the split oxygen could not be located unambiguously in the succeeding difference map.

Before the two final least-squares cycles, three reflections apparently suffering secondary extinction were given zero weight in the refinement. The final agreement factor is 0.038. Structure factor calculations were based on the following scattering curves: sulfur, Dawson;[7] sodium ion, Boys;[8] oxygen, nitrogen, and carbon, Berghuis, *et al.*;[9] hydrogen, Stewart, *et al.*[10]

## Results

Final atomic coordinates and thermal parameters are given in Tables I and II. Bond lengths and angles calculated from these parameters are listed in Tables III and IV. Figure 1 shows the molecular packing in the crystal viewed along the $c$ axis. The interplanar spacing between partially overlapping pyrimidine rings is half the unit translation along $c$, 3.473 Å, which is

---

(5) (a) J. De Meulenaer and H. Tompa, *Acta Cryst.*, **19**, 1014 (1965). (b) The computer program originally written for the IBM 1620 computer has been modified for IBM 7094 by Dave Cullen.

(6) J. M. Stewart, Crystal Structure Calculation System, Computer Sciences Center, University of Maryland.

(7) B. Dawson, *Acta Cryst.*, **13**, 403 (1960).

(8) S. F. Boys "International Tables for X-ray Crystallography" Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(9) J. Berghuis, IJ. M. Haanappel, M. Potters, O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

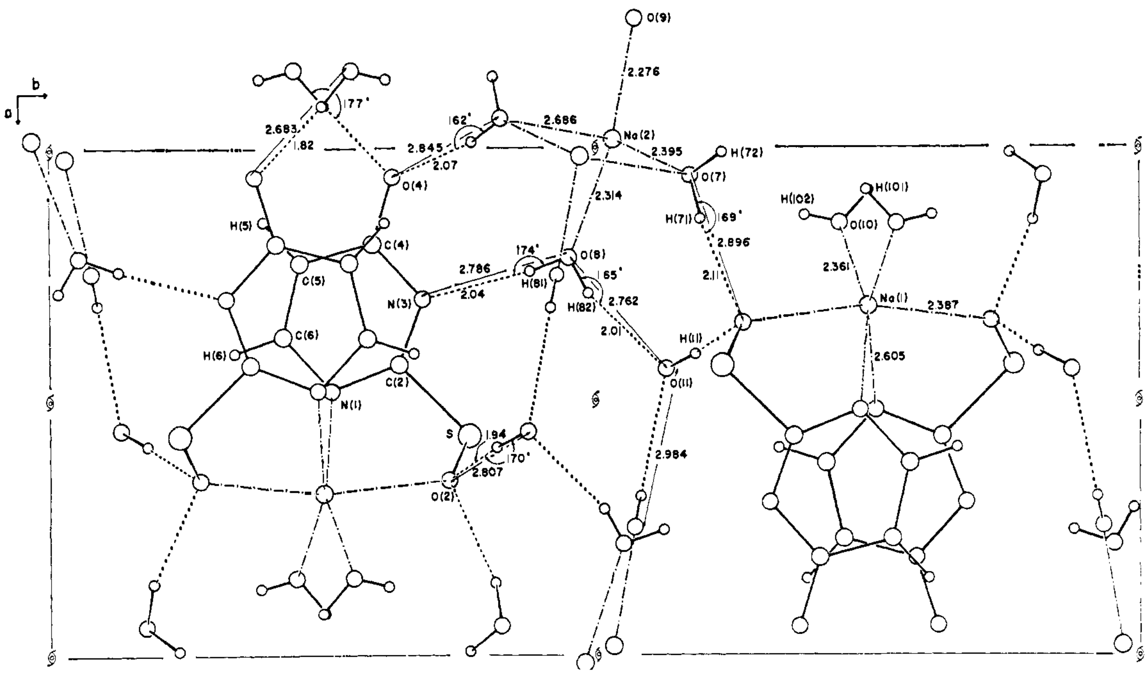


Figure 1. The structure viewed along the *c* axis.

somewhat longer than the spacing usually found in stacks of pyrimidine rings. The hydrogen bond acceptors O(2), O(4), and N(3) in the anion are linked to water molecules in a three-dimensional network of hydrogen bonds. In addition, ionic bonds are formed between the sodium ion Na(1) and atoms N(1) and O(2) in successive layers (Figure 2). The irregular coordination octahedron around Na(1) is completed by two water molecules related by a twofold axis. The other sodium ion, Na(2), is surrounded by six water molecules, four of which are interrelated either by a mirror plane or by a center of inversion. The water oxygen O(9) in this coordination octahedron is disordered (*cf.* Figure 2). Equivalent octahedra are stacked in columns parallel to the *c* axis. The distances between sodium ions in the two columns are 3.473 and 3.538 Å, respectively. Except for hydrogen bonds, ion–ion and ion–dipole bonds, there are no close intermolecular contacts in the structure.

**Table II.** Final Coordinates and Thermal Parameters for the Hydrogen Atoms

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| H(5) | 0.1465 (34) | 0.1942 (16) | 0.2500 (0) | 3.4 (8) |
| H(6) | 0.4040 (35) | 0.1678 (17) | 0.2500 (0) | 3.7 (8) |
| H(71) | 0.1412 (38) | 0.5941 (16) | 0.5260 (58) | 9.1 (1.2) |
| H(72) | 0.0111 (34) | 0.6149 (16) | 0.5585 (50) | 7.4 (1.1) |
| H(81) | 0.2440 (46) | 0.4383 (46) | 0.2500 (0) | 5.4 (1.2) |
| H(82) | 0.2884 (52) | 0.4925 (24) | 0.2500 (0) | 7.6 (1.7) |
| H(101) | 0.0818 (45) | 0.7513 (23) | 0.2500 (0) | 5.7 (1.3) |
| H(102) | 0.1334 (53) | 0.6927 (23) | 0.2500 (0) | 6.0 (1.8) |
| H(111) | 0.4074 (39) | 0.5903 (18) | 0.3414 (62) | 12.0 (1.6) |

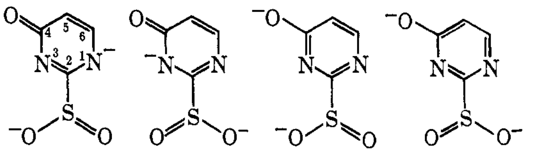
## Discussion

There is little doubt that a disulfide was originally isolated from the thiouracil–iodine reaction mixture. The reaction product appeared to be identical with that described by Miller, *et al.*[3] The scission of the sulfur–sulfur bond and the subsequent oxidation to sulfinate probably occurred during the slow recrystallization from the water–acetone solution.

**Table III.** Interatomic Distances with the Corresponding Standard Deviations in Parentheses

| Bond | Distance, Å | Bond | Distance, Å |
|---|---|---|---|
| | Dianion and Water Molecules | | |
| N(1)-C(2) | 1.323 (4) | C(5)-H(5) | 1.02 (3) |
| C(2)-N(3) | 1.321 (4) | C(6)-H(6) | 0.93 (3) |
| N(3)-C(4) | 1.371 (4) | O(7)-H(71) | 0.80 (4) |
| C(4)-C(5) | 1.419 (4) | O(7)-H(72) | 0.81 (3) |
| C(5)-C(6) | 1.351 (5) | O(8)-H(81) | 0.75 (4) |
| C(6)-N(1) | 1.363 (4) | O(8)-H(82) | 0.77 (5) |
| C(2)-S | 1.835 (3) | O(10)-H(101) | 0.87 (4) |
| S-O(2) | 1.516 (2) | O(10)-H(102) | 0.64 (5) |
| C(4)-O(4) | 1.274 (4) | O(11)-H(111) | 0.88 (4) |
| | Surroundings of the Sodium Ions | | |
| Na(1)-N(1)(i) | 2.605 (2) | Na(2)-O(7) | 2.395 (3) |
| Na(1)-O(2)(i) | 2.387 (2) | Na(2)-O(7)(ii) | 2.686 (3) |
| Na(1)-O(10) | 2.361 (2) | Na(2)-O(8) | 2.314 (4) |
| | | Na(2)-O(9) | 2.276 (5) |

The pyrimidinesulfinate ion is formally doubly negative, and may be described in terms of resonance between the valence bond structures I–IV. The bond lengths C(2)–N(1) and C(2)–N(3) are equal to within one standard deviation, indicating that the four valence bond structures displayed above are equally important. The corresponding bond lengths in uracil[11] are also



I II III IV

---

(11) R. F. Stewart and L. H. Jensen, *Acta Cryst.*, 23, 1102 (1967).

Table IV. Interatomic Angles and Corresponding Standard Deviations[a]

| Atoms | Angles, deg | Atoms | Angles, deg | Atoms | Angles, deg |
|---|---|---|---|---|---|
| Dianion and Water Molecules | | | | | |
| C(6)-N(1)-C(2) | 112.9 (3) | C(5)-C(4)-O(4) | 123.6 (3) | C(5)-C(6)-H(6) | 123 (2) |
| N(1)-C(2)-N(3) | 129.7 (3) | C(4)-C(5)-C(6) | 118.9 (3) | N(1)-C(6)-H(6) | 113 (2) |
| N(1)-C(2)-S | 115.9 (2) | C(5)-C(6)-N(1) | 123.8 (3) | H(71)-O(7)-H(72) | 109 (3) |
| N(3)-C(2)-S | 114.4 (2) | C(2)-S-O(2) | 100.6 (1) | H(81)-O(8)-H(82) | 101 (5) |
| C(2)-N(3)-C(4) | 117.2 (3) | O(2)-S-O(2)(iii) | 108.4 (1) | H(101)-O(10)-H(102) | 116 (2) |
| N(3)-C(4)-C(5) | 117.5 (3) | C(4)-C(5)-H(5) | 115 (2) | H(111)-O(11)-H(111)(iii) | 93 (4) |
| N(3)-C(4)-O(4) | 118.8 (3) | C(6)-C(5)-H(5) | 126 (2) | | |
| Surroundings of the Sodium Ions | | | | | |
| N(1)(i)-Na(1)-O(2)(i) | 73.2 (1) | O(2)(i)-Na(1)-O(10) | 90.8 (1) | O(7)-Na(2)-O(8) | 87.7 (1) |
| N(1)(i)-Na(1)-O(2)(iv) | 95.6 (1) | O(2)(i)-Na(1)-O(10)(v) | 98.6 (1) | O(7)-Na(2)-O(9) | 90.8 (2) |
| N(1)(i)-Na(1)-N(1)(iv) | 83.9 (1) | O(10)-Na(1)-O(10)(v) | 100.9 (1) | O(8)-Na(1)-O(7)(ii) | 81.9 (1) |
| N(1)(i)-Na(1)-O(10) | 162.1 (1) | O(7)-Na(2)-O(7)(ii) | 91.9 (1) | O(8)-Na(1)-O(9) | 164.6 (2) |
| N(1)(i)-Na(1)-O(10)(v) | 89.8 (1) | O(7)-Na(2)-O(7)(iii) | 97.1 (1) | O(9)-Na(1)-O(7)(ii) | 82.9 (2) |
| O(2)(i)-Na(1)-O(2)(iv) | 165.2 (1) | O(7)-Na(2)-O(7)(vi) | 165.9 (1) | O(9)-Na(1)-O(7)(v) | 96.8 (2) |

[a] Symmetry code: (i): $1 - x, 1 - y, 1 - z$; (ii): $-x, 1 - y, 1 - z$; (iii): $x, y, {}^1/_2 - z$; (iv): $1 - x, y + {}^1/_2, z$; (v): $x, {}^3/_2 - y, 1 - z$; (vi): $-x, 1 - y, z - {}^1/_2$.

equal, while in 2,4-dithiouracil[12] the C(2)–N(3) bond is 0.06 Å longer than C(2)–N(1). This change, brought about by replacing oxygen by sulfur in the 4 position, is difficult to explain by simple valence bond theory. Molecular orbital calculation on 2,4-dithiouracil[13] also fails to give a qualitatively correct description, predicting C(2)–N(3) to be slightly *shorter* than C(2)–N(1).

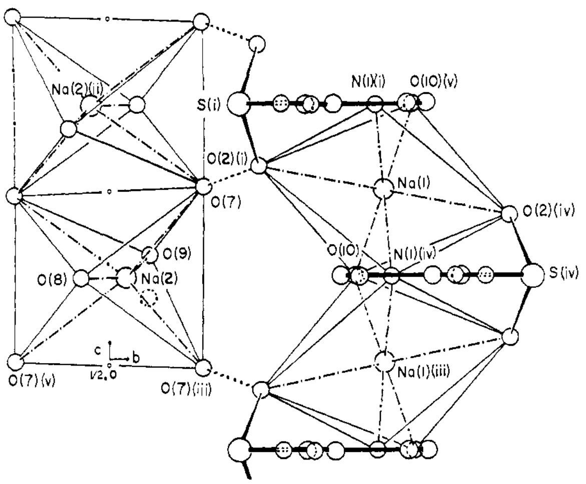


Figure 2. The environment of the sodium ions as viewed along the *a* axis.

The carbonyl bond length of 1.274 Å agrees with the predicted value of 1.27 Å for the carbon–oxygen bond in a carboxylate ion,[14] supporting the idea of equal contributions from each of the four valence bond structures above. In uracil the C=O bond at the 2 position is essentially a pure double bond (1.215 Å) while the C=O bond at the 4 position is significantly longer (1.245 Å). The carbonyl oxygen in the present structure participates in two hydrogen bonds, while in uracil the oxygen at the 4 position forms only one hydrogen bond and the oxygen at the 2 position none. This indicates that some of the lengthening of the C=O bond may be caused by hydrogen bonding.

In none of the more probable valence bond structures does the carbon–sulfur bond occur as a double bond. Thus the observed distance of 1.835 Å should represent a nearly pure $C_{sp^2}$–S(IV) single bond. Usually, the length of a carbon–sulfur single bond is taken as 1.82 Å.[15] However, in a number of structures considerably longer C–S bonds have been observed, *e.g.*, in L-cystine hydrochloride[16] $C_{sp^3}$–S(II) = 1.865 Å, in 2,5-dimethyl-2,5-*endo*-thio-1,4-dithiane[17] 1.845 and 1.850 Å, and in the cyclic adduct from 3-diazobutanone and carbon disulfide[18] 1.849 and 1.911 Å. In the latter structure, the carbon–sulfur bonds are part of a four-membered ring and the extraordinary lengthening might be due to appreciable nonbonded interaction. This suggests that the single bond radius of sulfur depends to a certain degree on the number and the nature of the groups bonded to the sulfur.

$C_{sp^2}$–S(VI) single bonds in most sulfonates are found to be close to 1.77 Å, while in the present structure the $C_{sp^2}$–S (IV) bond is 1.835 Å. The replacement of one oxygen in the sulfonate group by a lone pair is supposed to lower the effective nuclear charge for the d orbitals with a loss of bonding strength.[19] If it is assumed that the sulfur $\sigma$ orbital has an admixture of d character, the shielding effect of the lone pair may explain the lengthening of the C–S bond.

The two symmetry-related sulfinate oxygens in the present structure are both coordinated to sodium ions and the observed S–O bond length is 1.516 Å. In sodium hydroxymethanesulfinate[20] where only one of the sulfinate oxygens is coordinated to sodium, the S–O bonds are slightly different (1.495 and 1.511 Å). Sulfur–oxygen bond lengths in sulfonates are found in the range 1.44 ± 0.02 Å, and the relative lengthening of the S–O bonds observed in sulfinates are in accord-

---

(12) E. Shefter and H. G. Mautner, *J. Am. Chem. Soc.*, **89**, 1249 (1967).

(13) H. G. Mautner and G. Bergson, *Acta Chem. Scand.*, 17, 1694 (1963).

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 275.

(15) S. C. Abrahams, *Quart. Rev.* (London), **10**, 407 (1956).

(16) L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Am. Chem. Soc.*, **80**, 3835 (1958).

(17) A. M. O'Connell, *Acta Cryst.*, **23**, 623 (1967).

(18) J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Am. Chem. Soc.*, **90**, 5800 (1968).

(19) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(20) M. R. Truter, *ibid.*, 3064 (1955).

ance with the theory applied to the C–S bonds. The sodium-coordinated S–O bonds are slightly longer than the noncoordinated S–O bond; however, this difference is hardly significant.

**Acknowledgment.** The author wishes to thank Dr. Lyle H. Jensen for helpful discussions. Financial support under Grant AM-3288 from the National Institutes of Health is also gratefully acknowledged.

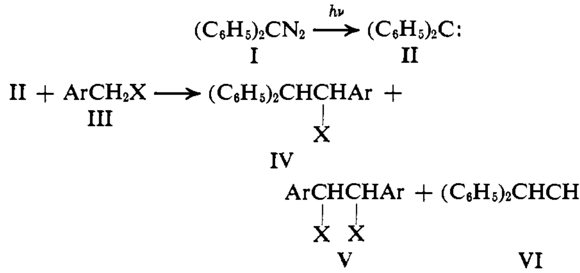
# *Communications to the Editor*

## Induced Dynamic Nuclear Spin Polarization in Reactions of Photochemically and Thermally Generated Triplet Diphenylmethylene[1]

*Sir:*

Several examples of chemically induced dynamic nuclear spin polarization in free radical reactions have been reported.[2] Although no detailed theoretical treatment has been published, a specific mechanism has been proposed to account qualitatively for the observed phenomenon.[2a,3,4] We wish to report the first examples of strong nuclear polarizations resulting from photochemically initiated reactions proceeding through triplet-state intermediates.[5]

Diphenyldiazomethane (I) decomposes photochemically to diphenylmethylene (II), shown by esr spectroscopy to have a triplet ground state.[6] In solvents with benzylic hydrogens (III) the reaction products are triarylethanes (IV), diarylethanes (V), and tetraphenylethane (VI).[7] When a solution of I (1.5% w/v) in toluene (IIIa) was irradiated inside the probe of an nmr spectrometer which had been modified to admit the focused light beam of an Osram 500-W super-high-pressure mercury arc, the spectrum shown in Figure 1$\beta$ was obtained. Transitions 1–8 are true photo-signals as shown by their collapse within a few seconds after irradiation was ceased, leaving only the methyl-$^{13}C$ peak of toluene as shown in Figure 1$\alpha$. The signals were regenerated immediately after the light was readmitted. After all diphenyldiazomethane had been consumed (~8-min irradiation) spectrum $\gamma$ was obtained. Lines 1–8 correspond in chemical shifts and coupling constant to the $A_2B$ spectrum of the benzylic protons in 1,1,2-triphenylethane (IVa). Lines a and b in Figure 1$\beta$ and 1$\gamma$ are caused by the benzylic protons of Va and VI, respectively. Equivalently polarized spectra were obtained with mesitylene (IIIb). Solvents with benzylic methylene groups such as methyl phenylacetate (IIIc) and benzyl cyanide (IIId) also gave strongly polarized spectra originating from IVc and IVd, respectively. In the latter compounds the benzylic protons give AB quartets with positive polarizations of lines 1 and 3 and negative polarization for transitions 2 and 4 (labeling the transitions in a sequence of increasing field).



$$\underset{\text{I}}{(C_6H_5)_2CN_2} \xrightarrow{h\nu} \underset{\text{II}}{(C_6H_5)_2C:}$$

$$\text{II} + \underset{\text{III}}{ArCH_2X} \longrightarrow \underset{\text{IV}}{(C_6H_5)_2CH\underset{X}{C}HAr} + \underset{\text{V}}{Ar\underset{X}{C}H\underset{X}{C}HAr} + \underset{\text{VI}}{(C_6H_5)_2CHCH(C_6H_5)_2}$$

a, Ar = $C_6H_5$; X = H
b, Ar = 3,5-$(CH_3)_2C_6H_3$; X = H
c, Ar = $C_6H_5$; X = $COOCH_3$
d, Ar = $C_6H_5$; X = CN

The polarization ($P$) is defined as $P = (\langle I_z\rangle - \langle I_z\rangle_0)/\langle I_z\rangle_0$ where $\langle I_z\rangle$ and $\langle I_z\rangle_0$ are the expectation values of the nuclear spins in the polarized states and at thermoequilibrium.[8,9] At sufficiently high concentrations (>1% w/v) the photochemical reaction rate is independent of the concentration of I, and the steady-state concentration of polarized IVa is given by $[\text{IVa}^*]_s = nk_LT_1$, where $k_L$ is the zero-order rate for the decomposition of I, $n$ is the fraction of IVa produced (yield), and $T_1$ is the nuclear spin lattice relaxation time of IVa. Independent measurements of these parameters ($n = 0.40$, $k_L = 4.0 \times 10^{-4}$ $M$ sec$^{-1}$, $T_1 = 2.2$ sec) gives $[\text{IVa}^*]_s = 3.53 \times 10^{-4}$ $M$. Intensity comparisons with a standard solution of IVa gives a polarization for lines 1 and 4 of $|P| = 760 \pm 100$.

Polarized spectra of IVb–*d* were also obtained by thermally decomposing I in IIIb–*d* at 140° (*e.g.*, Figure 2). The signal-to-noise ratios of these spectra were up to one order of magnitude larger than in the photochemical reaction because larger steady-state concentrations of polarized compounds were easily obtainable by increasing the concentration of I and accelerating the rate of its decomposition. The signs and relative intensities of the various transitions in the polarized spectra were identical with those obtained in the corresponding photochemical reactions.

---

[1] Work supported in part by National Science Foundation Grant GP-7043X.

[2] (a) J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1551, 1556 (1967); (b) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967); (c) H. R. Ward, R. G. Lawler, and H. Y. Loken, *ibid.*, **90**, 7361 (1968); H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969); (d) A. R. Lepley, *ibid.*, **90**, 2710 (1968); A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); (e) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

[3] R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5519 (1967).

[4] M. Cocivera, *ibid.*, **90**, 3261 (1968).

[5] Cocivera[4] observed nuclear polarizations originating from photoexcited states of certain quinones without net chemical reaction.

[6] For a summary of references, see G. L. Closs, "Topics of Stereochemistry," Vol. 3, John Wiley & Sons, Inc., New York, N. Y., 1968, pp 198–203.

[7] W. Kirmse and L. Horner, *Ann.*, **625**, 34 (1959).

[8] The polarization equals the spectra enhancement factor ($F$) when the radiofrequency field amplitude is not markedly altered by resonance of the polarized nuclei. That this condition is met can be seen by comparing the relative intensities of transitions 1 and 4 which, except for different signs, are the same as in the unpolarized compound.

[9] For a review on dynamic nuclear polarization, see K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance* 3, 79 (1968).