C(16)—C(17)	1.505 (7)	C(16)—C(18)	1.505 (4)
C(19)—C(20)	1.521 (5)	C(20)—C(21)	1.520 (5)
C(21)—C(22)	1.511 (6)		

C(1)—O(2)—C(5)	109.1 (2)	C(14)—O(3)—C(18)	110.1 (2)
C(10)—N—C(13)	109.3 (2)	C(10)—N—C(19)	123.1 (2)
C(13—N—C(19)	115.9 (2)	O(1)—C(1)—O(2)	121.6 (3)
O(1)—C(1)—C(2)	128.3 (3)	O(2)—C(1)—C(2)	110.1 (3)
C(1)—C(2)—C(3)	112.5 (3)	C(1)—C(2)—C(4)	101.4 (2)
C(3)—C(2)—C(4)	120.6 (2)	C(2)—C(4)—C(5)	100.7 (2)
C(2)—C(4)—C(11)	110.9 (2)	C(5)—C(4)—C(11)	113.7 (2)
O(2)—C(5)—C(4)	103.3 (2)	O(2)—C(5)—C(6)	109.9 (2)
C(4)—C(5)—C(6)	118.1 (2)	C(5)—C(6)—C(7)	111.4 (3)
C(5)—C(6)—C(9)	111.1 (2)	C(7)—C(6)—C(9)	112.3 (3)
C(6)—C(7)—C(8)	114.8 (3)	C(6)—C(9)—C(10)	113.5 (2)
C(6)—C(9)—C(22)	116.4 (3)	C(10)—C(9)—C(22)	112.6 (2)
N—C(10)—C(9)	120.2 (2)	N—C(10)—C(11)	105.4 (2)
C(9)—C(10)—C(11)	113.5 (2)	C(4)—C(11)—C(10)	115.5 (2)
C(4)—C(11)—C(12)	111.8 (2)	C(10)—C(11)—C(12)	101.8 (2)
C(11)—C(12)—C(13)	103.2 (2)	N—C(13)—C(12)	104.4 (2)
N—C(13)—C(14)	114.3 (2)	C(12)—C(13)—C(14)	109.6 (2)
O(3)—C(14)—C(13)	110.1 (2)	O(3)—C(14)—C(15)	103.5 (2)
C(13)—C(14)—C(15)	115.3 (2)	C(14)—C(15)—C(16)	104.0 (3)
C(15)—C(16)—C(17)	116.5 (4)	C(15)—C(16)—C(18)	102.5 (2)
C(17)—C(16)—C(18)	114.2 (3)	O(3)—C(18)—O(4)	120.7 (3)
O(3)—C(18)—C(16)	110.5 (3)	O(4)—C(18)—C(16)	128.8 (3)
N—C(19)—C(20)	114.1 (3)	C(19)—C(20)—C(21)	114.5 (3)
C(20)—C(21)—C(22)	115.4 (3)	C(9)—C(22)—C(21)	116.8 (3)

C(10)—N—C(19)—C(20)	64.4 (5)
C(19)—C(20)—C(21)—C(22)	63.8 (6)
C(21)—C(22)—C(9)—C(10)	77.7 (5)
C(9)—C(10)—N—C(19)	−1.3 (5)
N—C(19)—C(20)—C(21)	−80.1 (5)
C(20)—C(21)—C(22)—C(9)	−64.7 (5)
C(22)—C(9)—C(10)—N	−60.1 (5)

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). H atoms were located in a difference Fourier synthesis using *Xtal* (Stewart & Hall, 1983).

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References

Bocian, D. F. & Strauss, H. L. (1977). *J. Am. Chem. Soc.* **99**, 2866–2882.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Edwards, O. E., Feniak, G. & Handa, K. L. (1962). *Can. J. Chem.* **40**, 455–462.

Götz, M., Bögri, T. & Gray, A. H. (1961). *Tetrahedron Lett.* pp. 707–715.

Götz, M., Bögri, T., Gray, A. H. & Strunz, G. M. (1968). *Tetrahedron*, **24**, 2631–2643.

Harada, H., Irie, H., Masaki, N., Osaki, K. & Uyeo, S. (1967). *Chem. Commun.* pp. 460–462.

Keller, E. (1988). *SCHAKAL*88. *Fortran Program for the Graphic Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.

Lobstein, J. E. & Grumbach, J. (1932). *C. R. Acad. Sci.* **194**, 386–389.

Schild, H. (1936). *Chem. Ber.* **69**, 74–80.

Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Stewart, J. M. & Hall, S. R. (1983). Editors. *The Xtal System of Crystallographic Programs*. Technical Report TR-1364.2. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Stoddart, J. E. (1971). *Stereochemistry of Carbohydrates*, pp. 102–104. New York: John Wiley.

Suzuki, K. (1934). *J. Pharm. Soc. Jpn*, **54**, 573–579.

Thanh Ky, P., Ngoc Kim, V. & Xuan Dung, N. (1991). *Tap Chi Duoc Hoc*, **5**, 4–5.

Interactions Between Sulfonated Azo Dyes and Biomolecules: Orange G/Adenine and Orange G/Cytosine Salts

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Abstract

The disulfonated azo dye Orange G [the disodium salt of 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid] forms salts with adenine and cytosine on co-crystallization from aqueous HCl. The 1:2 dye:adenine crystal, $2C_5H_6N_5^+.C_{16}H_{10}N_2O_7S_2^{2-}.5H_2O$, is a pentahydrate and the 1:2 dye:cytosine crystal, $2C_4H_6N_3O^+.C_{16}H_{10}N_2O_7S_2^{2-}.H_2O$, is a monohydrate. In the solid state the dye is found to exist predominantly as the hydrazo, rather than the azo, tautomer. In both structures, one of the protonated nucleotide bases approaches close to a sulfonate group of the dye in an 'edge-on' fashion. Molecules in the Orange G/adenine structure lie in segregated layers, but molecules in the Orange G/cytosine structure lie in mixed stacks.

Comment

Interactions between biomolecules containing sulfate groups and biomolecules (such as proteins) capable of recognizing these groups are currently the object of intensive biomedical study. Although the focus of

such investigations is often on large sulfated molecules such as heparin, we are currently studying interactions between smaller molecules, particularly between *sulfonated* azo dyes and biomolecules, such as amino acids and nucleic acid bases, to determine whether the sulfonate group can serve as a mimic of the sulfate group. Sulfonated azo dyes have proved effective as co-precipitating and co-crystallizing agents for peptides and other biomolecules (Conroy & Lovrien, 1992). In addition, these dyes are of special interest in their own right because their potential usefulness as pharmaceuticals, especially as antiviral agents, has recently been recognized (Weaver, Pine, Anand, Bell & Aszalos, 1992). Understanding the biological activity of sulfated/sulfonated compounds and modeling their interactions with proteins or nucleic acids is greatly facilitated by the availability of structural information from X-ray crystallographic studies. Here we describe the structures of two crystalline dye/biomolecule salts grown from $0.2\ N$ HCl solution, one consisting of the dye Orange G and adenine, the other consisting of Orange G and cytosine.

Orange G Dianion

azo ⇌ hydrazo

Adenine

Cytosine

In each crystal structure the asymmetric unit was found to contain one dye molecule (as the dianion) and two protonated nucleotide base molecules (Figs. 1 and 2). Location of the corresponding H atoms in difference maps identified the protonation sites as the ring N atoms adjacent to the amino groups for both adenine and cytosine. The asymmetric unit of Orange G/adenine also contains five water molecules, while that of Orange G/cytosine contains only a single water molecule.

The geometry of the dye molecule in both structures is of interest in several respects. An azo compound with a suitably placed naphtholic hydroxyl group may exist as a hydrazone, as an azo compound, or as an equilibrium mixture of the two tautomers either in solution or in the solid state
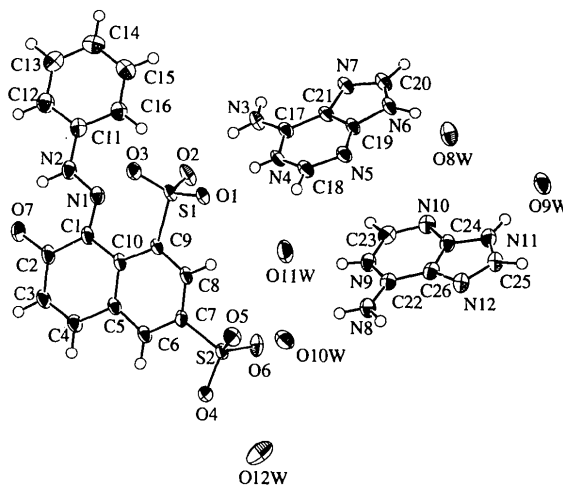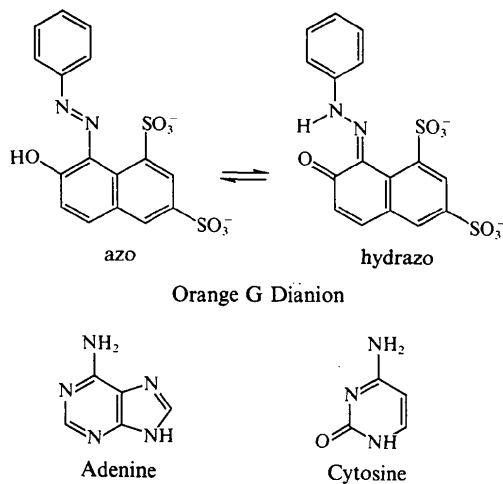

Fig. 1. View of the Orange G/adenine asymmetric unit, showing atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

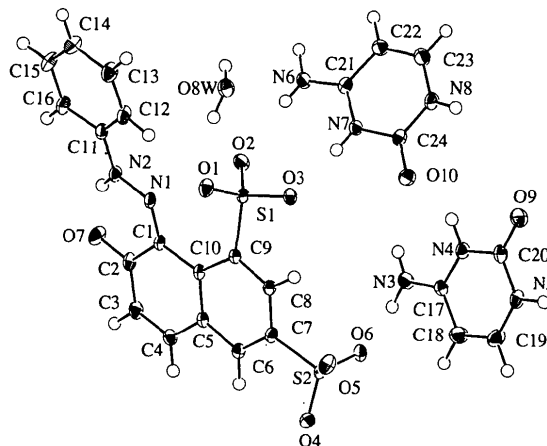Fig. 2. View of the Orange G/cytosine asymmetric unit, showing atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

(Olivieri, Wilson, Paul & Curtin, 1989). In the crystal structures described here, the location of the H atom on N(2) rather than on O(7) and the lengths of the N(1)—N(2), N(1)—C(1), and C(2)—O(7) bonds indicate that here Orange G exists primarily as the hydrazo tautomer rather than as the azo tautomer. In both structures the S(1)—C(9) bond is significantly longer than the S(2)—C(7) bond, perhaps as a result of crowding by the bulky phenylazo substituent located near the S(1) sulfonate group. We have also observed this bond-length difference in the crystal structures of the diammonium, dilithium, magnesium, and calcium salts of Orange G (Ojala *et al.*, 1994). In Orange G/adenine and Orange G/cytosine the conformations of the dye molecules resemble each other closely, with the phenylazo groups assum-

ing almost identical orientations with respect to the naphthalene rings. Corresponding torsion angles describing the geometry of the phenylazo groups are very similar (Tables 3 and 4).

Noteworthy among the many hydrogen bonds in the structures (Table 5) are contacts between two of the O atoms from a given sulfonate group and two N—H groups from a neighboring protonated nucleotide base molecule. This two-pronged sulfonate-bridging contact, found in both crystal structures [O(1)···N(4) = 2.742 (4), O(2)···N(3) = 2.809 (4) Å in Orange G/adenine; O(2)···N(6) = 2.857 (2), O(3)···N(7) = 2.740 (2) Å in Orange G/cytosine], is suggestive of the type of contact expected between a sulfonate group (or sulfate group) and the guanidinium terminus of an arginine side chain, an interaction likely to occur between sulfonated (or sulfated) molecules and peptides. In both structures the interacting O—S—O and N—C—N groups approach each other in approximately the same plane [the angle between the planes O(1)—S(1)—O(2) and N(3)—C(17)—N(4) in Orange G/adenine is 18.3 (3)°; the angle between the planes O(2)—S(1)—O(3) and N(6)—C(21)—N(7) in Orange G/cytosine is 26.3 (2)°].

Inspection of the packing arrangements assumed in these two structures reveals a striking difference between adenine and cytosine molecules with respect to how they interact with and are packed with the molecules of Orange G. Orange G and adenine molecules do not mingle freely in the crystal but instead lie in segregated layers (Fig. 3). The water molecules present in the structure are found in the regions where these layers meet and into which the sulfonate groups project. In contrast, a neatly segregated layer structure is not found in Orange G/cytosine. Instead the molecules lie in stacks in which cytosine and Orange G molecules overlap (Fig. 4). In these crystal structures, at least, the sulfonated azo dye appears to intercalate more readily with cytosine molecules than with adenine molecules.

Fig. 4. View of the Orange G/cytosine molecular packing, showing mixed stacks of dye and nucleotide base molecules. H atoms (except those on the cytosine amino groups) have been omitted for clarity.

Experimental

Co-precipitation and co-crystallization techniques used for growing these and similar co-crystals have been described previously (Conroy & Lovrien, 1992).

Orange G/Adenine

Crystal data

$2C_5H_6N_5^+.C_{16}H_{10}N_2O_7S_2^{2-}.$	Cu $K\alpha$ radiation
$5H_2O$	$\lambda = 1.54178$ Å
$M_r = 768.73$	Cell parameters from 25
Triclinic	reflections
$P\bar{1}$	$\theta = 20.0-25.0°$
$a = 10.157$ (4) Å	$\mu = 2.18$ mm^{-1}
$b = 10.277$ (6) Å	$T = 173$ K
$c = 17.551$ (6) Å	Thin plate
$\alpha = 92.81$ (4)°	$0.36 \times 0.12 \times 0.02$ mm
$\beta = 93.07$ (3)°	Orange
$\gamma = 118.00$ (5)°	
$V = 1609$ (3) Å^3	
$Z = 2$	
$D_x = 1.586$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.064$
diffractometer	$\theta_{max} = 70.0°$
$\omega/2\theta$ scans	$h = -12 \rightarrow 12$
Absorption correction:	$k = -12 \rightarrow 12$
empirical	$l = -17 \rightarrow 21$
$T_{min} = 0.80$, $T_{max} = 1.00$	3 standard reflections
9379 measured reflections	frequency: 60 min
6026 independent reflections	intensity variation: none
4785 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

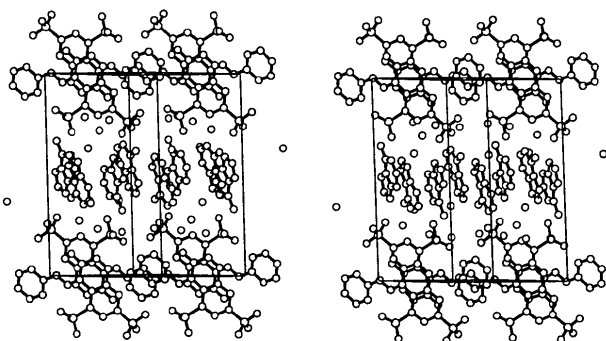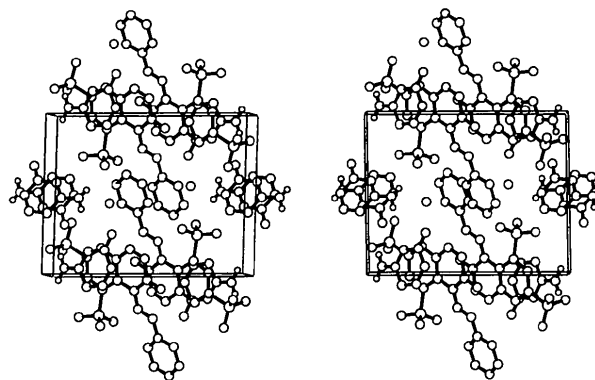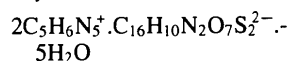|	
Refinement on F	$\Delta\rho_{max} = 0.65$ e Å^{-3}
$R = 0.055$	$\Delta\rho_{min} = -0.65$ e Å^{-3}
$wR = 0.075$	Extinction correction:
$S = 2.68$	not applied

Fig. 3. View of the Orange G/adenine molecular packing, showing alternating layers of dye and nucleotide base molecules. H atoms have been omitted for clarity.

4785 reflections
496 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.02$

Orange G/Cytosine

Crystal data

$2C_4H_6N_3O^+.C_{16}H_{10}N_2O_7S_2^{2-}$.-
H_2O
$M_r = 648.62$
Triclinic
$P\bar{1}$
$a = 8.908$ (2) Å
$b = 11.632$ (4) Å
$c = 13.697$ (2) Å
$\alpha = 90.17$ (3)°
$\beta = 90.74$ (2)°
$\gamma = 110.96$ (2)°
$V = 1325$ (1) Å^3
$Z = 2$
$D_x = 1.625$ Mg m^{-3}

Data collection

Enraf–Nonius CAD-4
  diffractometer
$\omega/2\theta$ scans
Absorption correction:
  empirical
  $T_{min} = 0.77$, $T_{max} = 1.00$
9870 measured reflections
5020 independent reflections
4338 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.067$

Refinement

Refinement on F
$R = 0.034$
$wR = 0.048$
$S = 2.02$
4338 reflections
431 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25
  reflections
$\theta = 20.0$–$25.0°$
$\mu = 2.44$ mm^{-1}
$T = 173$ K
Thin plate
$0.36 \times 0.16 \times 0.04$ mm
Orange

$\theta_{max} = 70°$
$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections
  frequency: 60 min
  intensity variation: -5.6%
  (linear correction
  applied)

Extinction correction:
  isotropic
  (Zachariasen, 1963)
Extinction coefficient:
  0.44323×10^{-5}
Atomic scattering factors
  from *International Tables
  for X-ray Crystallography*
  (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for Orange G/adenine*

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
S(1)	0.27564 (8)	0.63144 (9)	0.20474 (4)	1.97 (2)
S(2)	−0.03967 (8)	0.9206 (1)	0.23031 (4)	1.95 (2)
O(1)	0.3035 (2)	0.7057 (3)	0.2822 (1)	2.16 (7)
O(2)	0.1767 (3)	0.4737 (3)	0.2054 (1)	2.94 (8)
O(3)	0.4151 (3)	0.6699 (3)	0.1709 (1)	2.56 (8)
O(4)	−0.0866 (3)	1.0100 (3)	0.1862 (1)	2.89 (9)
O(5)	0.0804 (3)	1.0081 (3)	0.2897 (1)	2.59 (8)
O(6)	−0.1628 (3)	0.7966 (3)	0.2612 (1)	3.07 (8)
O(7)	0.2449 (3)	0.5869 (3)	−0.1159 (1)	3.15 (9)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for Orange G/cytosine*

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
O(8W)	0.1040 (3)	0.5072 (3)	0.7217 (1)	3.5 (1)
O(9W)	−0.7767 (3)	−0.1925 (3)	0.6322 (1)	3.3 (1)
O(10W)	−0.4160 (3)	0.5226 (3)	0.2358 (1)	3.19 (9)
O(11W)	−0.4090 (3)	0.2053 (4)	0.2273 (1)	3.9 (1)
O(12W)	−0.3694 (3)	0.9698 (4)	0.2140 (2)	5.1 (1)
N(1)	0.2364 (3)	0.5229 (3)	0.0397 (1)	2.06 (8)
N(2)	0.2844 (3)	0.4558 (3)	−0.0069 (1)	2.27 (9)
N(3)	0.1363 (3)	0.3002 (4)	0.3296 (2)	2.5 (1)
N(4)	0.1948 (3)	0.5235 (3)	0.3979 (2)	2.17 (9)
N(5)	0.1780 (3)	0.5589 (3)	0.5306 (1)	2.29 (9)
N(6)	0.0860 (3)	0.3243 (3)	0.5883 (1)	2.30 (9)
N(7)	0.0572 (3)	0.1722 (3)	0.4845 (1)	2.28 (9)
N(8)	−0.4896 (3)	0.4074 (3)	0.3813 (2)	2.40 (9)
N(9)	−0.5629 (3)	0.1589 (3)	0.3524 (1)	2.20 (9)
N(10)	−0.6615 (3)	−0.0313 (3)	0.4365 (2)	2.5 (1)
N(11)	−0.6711 (3)	0.0697 (3)	0.5632 (2)	2.5 (1)
N(12)	−0.5781 (3)	0.3102 (3)	0.5430 (2)	2.5 (1)
C(1)	0.2009 (3)	0.6229 (4)	0.0135 (2)	2.1 (1)
C(2)	0.1967 (4)	0.6477 (4)	−0.0673 (2)	2.4 (1)
C(3)	0.1313 (4)	0.7366 (4)	−0.0919 (2)	2.6 (1)
C(4)	0.0760 (3)	0.7967 (4)	−0.0414 (2)	2.4 (1)
C(5)	0.0830 (3)	0.7804 (4)	0.0401 (2)	2.0 (1)
C(6)	0.0240 (3)	0.8482 (4)	0.0878 (2)	2.0 (1)
C(7)	0.0366 (3)	0.8420 (4)	0.1662 (2)	1.84 (9)
C(8)	0.1156 (3)	0.7740 (4)	0.1966 (2)	1.9 (1)
C(9)	0.1745 (3)	0.7046 (3)	0.1508 (2)	1.77 (9)
C(10)	0.1538 (3)	0.7004 (4)	0.0688 (2)	1.9 (1)
C(11)	0.3166 (3)	0.3456 (4)	0.0171 (2)	2.2 (1)
C(12)	0.3728 (4)	0.2822 (4)	−0.0356 (2)	2.8 (1)
C(13)	0.4057 (4)	0.1730 (5)	−0.0142 (2)	3.1 (1)
C(14)	0.3818 (4)	0.1247 (4)	0.0587 (2)	3.1 (1)
C(15)	0.3247 (4)	0.1867 (4)	0.1102 (2)	2.9 (1)
C(16)	0.2908 (4)	0.2962 (4)	0.0903 (2)	2.5 (1)
C(17)	0.1460 (3)	0.3745 (4)	0.3942 (2)	2.0 (1)
C(18)	0.2094 (3)	0.6083 (4)	0.4623 (2)	2.3 (1)
C(19)	0.1296 (3)	0.4119 (4)	0.5287 (2)	2.1 (1)
C(20)	0.0446 (4)	0.1833 (4)	0.5585 (2)	2.4 (1)
C(21)	0.1107 (3)	0.3162 (4)	0.4657 (2)	2.1 (1)
C(22)	−0.5432 (3)	0.2724 (4)	0.4028 (2)	2.0 (1)
C(23)	−0.6175 (4)	0.0165 (4)	0.3695 (2)	2.5 (1)
C(24)	−0.6414 (3)	0.0817 (4)	0.4880 (2)	2.2 (1)
C(25)	−0.6314 (4)	0.2083 (4)	0.5930 (2)	2.6 (1)
C(26)	−0.5857 (3)	0.2287 (4)	0.4762 (2)	2.1 (1)
S(1)	0.53621 (4)	1.25003 (3)	0.74078 (2)	1.23 (1)
S(2)	0.22690 (4)	0.80763 (3)	0.89456 (2)	1.21 (1)
O(1)	0.4539 (1)	1.2890 (1)	0.66224 (8)	1.81 (4)
O(2)	0.7104 (1)	1.3114 (1)	0.74289 (8)	1.77 (4)
O(3)	0.4672 (1)	1.2602 (1)	0.83575 (8)	1.66 (4)
O(4)	0.1761 (1)	0.6777 (1)	0.86761 (8)	1.68 (4)
O(5)	0.0955 (1)	0.8527 (1)	0.90436 (9)	1.89 (4)
O(6)	0.3342 (1)	0.8382 (1)	0.98040 (8)	1.57 (4)
O(7)	0.8522 (2)	1.0787 (1)	0.45398 (9)	2.09 (4)
O(8W)	0.5542 (2)	1.5524 (1)	0.7039 (1)	2.24 (5)
O(9)	0.1285 (2)	1.2631 (1)	1.29381 (9)	2.07 (4)
O(10)	0.4421 (1)	1.3182 (1)	1.07561 (9)	1.94 (4)
N(1)	0.6892 (2)	1.2087 (1)	0.55561 (9)	1.28 (4)
N(2)	0.7869 (2)	1.2658 (1)	0.4876 (1)	1.43 (4)
N(3)	0.3103 (2)	1.0500 (2)	1.0718 (1)	1.88 (5)
N(4)	0.2141 (2)	1.1542 (1)	1.1838 (1)	1.42 (4)
N(5)	0.0070 (2)	1.0538 (2)	1.2882 (1)	1.77 (5)
N(6)	0.8574 (2)	1.5127 (2)	0.8743 (1)	1.86 (5)
N(7)	0.6475 (2)	1.4196 (1)	0.9766 (1)	1.37 (4)
N(8)	0.6302 (2)	1.4968 (1)	1.1302 (1)	1.65 (5)
C(1)	0.6726 (2)	1.0922 (2)	0.5761 (1)	1.23 (5)
C(2)	0.7487 (2)	1.0241 (2)	0.5177 (1)	1.49 (5)
C(3)	0.7011 (2)	0.8939 (2)	0.5306 (1)	1.61 (5)
C(4)	0.5905 (2)	0.8358 (2)	0.5974 (1)	1.46 (5)

C(5)	0.5197 (2)	0.9009 (2)	0.6610 (1)	1.22 (5)
C(6)	0.4122 (2)	0.8313 (2)	0.7317 (1)	1.32 (5)
C(7)	0.3476 (2)	0.8894 (2)	0.7973 (1)	1.27 (5)
C(8)	0.3893 (2)	1.0169 (2)	0.7938 (1)	1.31 (5)
C(9)	0.4938 (2)	1.0879 (1)	0.7249 (1)	1.12 (5)
C(10)	0.5622 (2)	1.0305 (2)	0.6537 (1)	1.14 (5)
C(11)	0.8004 (2)	1.3847 (2)	0.4584 (1)	1.42 (5)
C(12)	0.7114 (2)	1.4469 (2)	0.5018 (1)	1.79 (5)
C(13)	0.7323 (2)	1.5642 (2)	0.4717 (1)	2.10 (6)
C(14)	0.8420 (2)	1.6200 (2)	0.3991 (1)	2.14 (6)
C(15)	0.9287 (2)	1.5566 (2)	0.3554 (1)	2.01 (6)
C(16)	0.9087 (2)	1.4380 (2)	0.3842 (1)	1.72 (5)
C(17)	0.2074 (2)	1.0477 (2)	1.1403 (1)	1.51 (5)
C(18)	0.0892 (2)	0.9365 (2)	1.1731 (1)	2.30 (6)
C(19)	−0.0070 (2)	0.9454 (2)	1.2460 (1)	2.23 (6)
C(20)	0.1150 (2)	1.1639 (2)	1.2576 (1)	1.54 (5)
C(21)	0.7876 (2)	1.5120 (2)	0.9582 (1)	1.50 (5)
C(22)	0.8502 (2)	1.6053 (2)	1.0307 (1)	1.87 (5)
C(23)	0.7674 (2)	1.5942 (2)	1.1143 (1)	1.98 (6)
C(24)	0.5668 (2)	1.4059 (2)	1.0631 (1)	1.45 (5)

Table 3. Selected geometric parameters (Å, °) for Orange G/adenine

S(1)—O(1)	1.471 (2)	N(11)—C(24)	1.369 (4)
S(1)—O(2)	1.453 (3)	N(11)—C(25)	1.352 (5)
S(1)—O(3)	1.450 (3)	N(12)—C(25)	1.330 (5)
S(1)—C(9)	1.792 (4)	N(12)—C(26)	1.384 (5)
S(2)—O(4)	1.454 (4)	C(1)—C(2)	1.455 (4)
S(2)—O(5)	1.457 (2)	C(1)—C(10)	1.462 (5)
S(2)—O(6)	1.458 (3)	C(2)—C(3)	1.428 (7)
S(2)—C(7)	1.763 (4)	C(3)—C(4)	1.344 (6)
O(7)—C(2)	1.279 (5)	C(4)—C(5)	1.450 (4)
N(1)—N(2)	1.298 (5)	C(5)—C(6)	1.391 (5)
N(1)—C(1)	1.332 (6)	C(5)—C(10)	1.416 (6)
N(2)—C(11)	1.395 (5)	C(6)—C(7)	1.382 (4)
N(3)—C(17)	1.309 (5)	C(7)—C(8)	1.390 (6)
N(4)—C(17)	1.367 (5)	C(8)—C(9)	1.382 (5)
N(4)—C(18)	1.350 (5)	C(9)—C(10)	1.438 (4)
N(5)—C(18)	1.320 (5)	C(11)—C(12)	1.398 (6)
N(5)—C(19)	1.350 (5)	C(11)—C(16)	1.397 (5)
N(6)—C(19)	1.366 (4)	C(12)—C(13)	1.375 (7)
N(6)—C(20)	1.372 (5)	C(13)—C(14)	1.387 (6)
N(7)—C(20)	1.316 (4)	C(14)—C(15)	1.380 (7)
N(7)—C(21)	1.380 (5)	C(15)—C(16)	1.377 (7)
N(8)—C(22)	1.314 (5)	C(17)—C(21)	1.408 (4)
N(9)—C(22)	1.358 (5)	C(19)—C(21)	1.386 (5)
N(9)—C(23)	1.356 (5)	C(22)—C(26)	1.409 (4)
N(10)—C(23)	1.315 (4)	C(24)—C(26)	1.373 (5)
N(10)—C(24)	1.365 (5)		

O(1)—S(1)—O(2)	110.5 (1)	C(7)—C(8)—C(9)	122.2 (3)
O(1)—S(1)—O(3)	111.0 (1)	S(1)—C(9)—C(8)	112.9 (2)
O(1)—S(1)—C(9)	104.5 (2)	S(1)—C(9)—C(10)	127.3 (3)
O(2)—S(1)—O(3)	114.9 (2)	C(8)—C(9)—C(10)	119.9 (3)
O(2)—S(1)—C(9)	106.8 (2)	C(1)—C(10)—C(5)	117.9 (3)
O(3)—S(1)—C(9)	108.5 (2)	C(1)—C(10)—C(9)	125.8 (4)
O(4)—S(2)—O(5)	112.8 (2)	C(5)—C(10)—C(9)	116.3 (3)
O(4)—S(2)—O(6)	113.7 (2)	N(2)—C(11)—C(12)	117.6 (3)
O(4)—S(2)—C(7)	106.6 (2)	N(2)—C(11)—C(16)	122.0 (4)
O(5)—S(2)—O(6)	111.3 (1)	C(12)—C(11)—C(16)	120.3 (4)
O(5)—S(2)—C(7)	105.8 (2)	C(11)—C(12)—C(13)	119.4 (3)
O(6)—S(2)—C(7)	106.0 (2)	C(12)—C(13)—C(14)	120.5 (4)
N(2)—N(1)—C(1)	119.0 (3)	C(13)—C(14)—C(15)	119.8 (5)
N(1)—N(2)—C(11)	121.0 (3)	C(14)—C(15)—C(16)	121.0 (4)
C(17)—N(4)—C(18)	124.8 (3)	C(11)—C(16)—C(15)	119.0 (4)
C(18)—N(5)—C(19)	111.8 (3)	N(3)—C(17)—N(4)	121.2 (3)
C(19)—N(6)—C(20)	106.4 (3)	N(3)—C(17)—C(21)	126.1 (4)
C(20)—N(7)—C(21)	102.8 (3)	N(4)—C(17)—C(21)	112.7 (3)
C(22)—N(9)—C(23)	124.4 (3)	N(4)—C(18)—N(5)	124.8 (3)
C(23)—N(10)—C(24)	111.4 (3)	N(5)—C(19)—N(6)	127.6 (3)
C(24)—N(11)—C(25)	105.9 (3)	N(5)—C(19)—C(21)	127.6 (3)
C(25)—N(12)—C(26)	102.9 (3)	N(6)—C(19)—C(21)	104.9 (3)
N(1)—C(1)—C(2)	122.6 (3)	N(6)—C(20)—N(7)	113.9 (3)
N(1)—C(1)—C(10)	117.0 (3)	N(7)—C(21)—C(17)	129.6 (3)
C(2)—C(1)—C(10)	120.2 (4)	N(7)—C(21)—C(19)	112.0 (3)
O(7)—C(2)—C(1)	121.0 (4)	C(17)—C(21)—C(19)	118.4 (3)
O(7)—C(2)—C(3)	120.5 (3)	N(8)—C(22)—N(9)	120.5 (3)
C(1)—C(2)—C(3)	118.4 (4)	N(8)—C(22)—C(26)	126.1 (3)
C(2)—C(3)—C(4)	120.7 (3)	N(9)—C(22)—C(26)	113.4 (3)
C(3)—C(4)—C(5)	123.0 (4)	N(9)—C(23)—N(10)	124.9 (3)
C(4)—C(5)—C(6)	118.7 (4)	N(10)—C(24)—N(11)	126.0 (4)
C(4)—C(5)—C(10)	119.1 (3)	N(10)—C(24)—C(26)	127.8 (3)
C(6)—C(5)—C(10)	122.2 (3)	N(11)—C(24)—C(26)	106.2 (3)
C(5)—C(6)—C(7)	120.2 (4)	N(11)—C(25)—N(12)	114.0 (3)
S(2)—C(7)—C(6)	122.9 (3)	N(12)—C(26)—C(22)	131.1 (3)
S(2)—C(7)—C(8)	118.1 (2)	N(12)—C(26)—C(24)	110.9 (3)
C(6)—C(7)—C(8)	119.0 (3)	C(22)—C(26)—C(24)	118.0 (3)

N(1)—N(2)—C(11)—C(12)	−177.8 (2)
N(2)—N(1)—C(1)—C(2)	7.5 (4)
C(1)—N(1)—N(2)—C(11)	−177.1 (2)

Table 4. Selected geometric parameters (Å, °) for Orange G/cytosine

S(1)—O(1)	1.456 (1)	N(8)—C(24)	1.355 (2)
S(1)—O(2)	1.458 (1)	C(1)—C(2)	1.456 (2)
S(1)—O(3)	1.468 (1)	C(1)—C(10)	1.463 (2)
S(1)—C(9)	1.798 (2)	C(2)—C(3)	1.431 (2)
S(2)—O(4)	1.459 (1)	C(3)—C(4)	1.347 (2)
S(2)—O(5)	1.451 (1)	C(4)—C(5)	1.443 (2)
S(2)—O(6)	1.466 (1)	C(5)—C(6)	1.409 (2)
S(2)—C(7)	1.775 (2)	C(5)—C(10)	1.421 (2)
O(7)—C(2)	1.273 (2)	C(6)—C(7)	1.372 (2)
O(9)—C(20)	1.219 (2)	C(7)—C(8)	1.396 (2)
O(10)—C(24)	1.224 (2)	C(8)—C(9)	1.384 (2)
N(1)—N(2)	1.295 (2)	C(9)—C(10)	1.439 (2)
N(1)—C(1)	1.341 (2)	C(11)—C(12)	1.387 (2)
N(2)—C(11)	1.404 (2)	C(11)—C(16)	1.397 (2)
N(3)—C(17)	1.313 (2)	C(12)—C(13)	1.375 (3)
N(4)—C(17)	1.355 (2)	C(13)—C(14)	1.393 (2)
N(4)—C(20)	1.381 (2)	C(14)—C(15)	1.385 (3)
N(5)—C(19)	1.350 (3)	C(15)—C(16)	1.385 (3)
N(5)—C(20)	1.368 (2)	C(17)—C(18)	1.423 (3)
N(6)—C(21)	1.312 (2)	C(18)—C(19)	1.352 (2)
N(7)—C(21)	1.351 (2)	C(21)—C(22)	1.423 (2)
N(7)—C(24)	1.374 (2)	C(22)—C(23)	1.351 (2)
N(8)—C(23)	1.358 (2)		

O(1)—S(1)—O(2)	114.65 (8)	C(6)—C(7)—C(8)	119.9 (1)
O(1)—S(1)—O(3)	110.87 (7)	C(7)—C(8)—C(9)	121.9 (1)
O(1)—S(1)—C(9)	107.57 (8)	S(1)—C(9)—C(8)	113.0 (1)
O(2)—S(1)—O(3)	111.06 (7)	S(1)—C(9)—C(10)	126.9 (1)
O(2)—S(1)—C(9)	107.56 (7)	C(8)—C(9)—C(10)	120.1 (1)
O(3)—S(1)—C(9)	104.50 (7)	C(1)—C(10)—C(5)	117.0 (1)
O(4)—S(2)—O(5)	114.08 (8)	C(1)—C(10)—C(9)	126.7 (1)
O(4)—S(2)—O(6)	112.33 (7)	C(5)—C(10)—C(9)	116.4 (1)
O(4)—S(2)—C(7)	105.78 (8)	N(2)—C(11)—C(12)	121.6 (1)
O(5)—S(2)—O(6)	111.85 (7)	N(2)—C(11)—C(16)	116.9 (1)
O(5)—S(2)—C(7)	107.23 (7)	C(12)—C(11)—C(16)	121.4 (2)
O(6)—S(2)—C(7)	104.80 (7)	C(11)—C(12)—C(13)	119.1 (2)
N(2)—N(1)—C(1)	119.0 (1)	C(12)—C(13)—C(14)	120.4 (2)
N(1)—N(2)—C(11)	121.4 (1)	C(13)—C(14)—C(15)	120.1 (2)
C(17)—N(4)—C(20)	125.3 (2)	C(14)—C(15)—C(16)	120.4 (2)
C(19)—N(5)—C(20)	122.6 (1)	C(11)—C(16)—C(15)	118.6 (2)
C(21)—N(7)—C(24)	124.3 (2)	N(3)—C(17)—N(4)	119.7 (2)
C(23)—N(8)—C(24)	122.3 (1)	N(3)—C(17)—C(18)	122.6 (2)
N(1)—C(1)—C(2)	121.8 (1)	N(4)—C(17)—C(18)	117.7 (1)
N(1)—C(1)—C(10)	117.7 (1)	C(17)—C(18)—C(19)	117.3 (2)
C(2)—C(1)—C(10)	120.2 (1)	N(5)—C(19)—C(18)	122.6 (2)
O(7)—C(2)—C(1)	120.6 (2)	O(9)—C(20)—N(4)	121.7 (2)
O(7)—C(2)—C(3)	120.4 (1)	O(9)—C(20)—N(5)	123.8 (1)
C(1)—C(2)—C(3)	119.0 (1)	N(4)—C(20)—N(5)	114.5 (2)
C(2)—C(3)—C(4)	120.5 (1)	N(6)—C(21)—N(7)	118.9 (2)
C(3)—C(4)—C(5)	122.3 (2)	N(6)—C(21)—C(22)	123.3 (2)
C(4)—C(5)—C(6)	117.2 (1)	N(7)—C(21)—C(22)	117.8 (1)
C(4)—C(5)—C(10)	120.6 (1)	C(21)—C(22)—C(23)	117.8 (2)
C(6)—C(5)—C(10)	122.1 (1)	N(8)—C(23)—C(22)	121.8 (2)
C(5)—C(6)—C(7)	119.7 (2)	O(10)—C(24)—N(7)	120.8 (2)
S(2)—C(7)—C(6)	121.1 (1)	O(10)—C(24)—N(8)	123.2 (1)
S(2)—C(7)—C(8)	118.7 (1)	N(7)—C(24)—N(8)	116.0 (2)

N(1)—N(2)—C(11)—C(12)	0.7 (2)
N(2)—N(1)—C(1)—C(2)	−6.3 (2)
C(1)—N(1)—N(2)—C(11)	175.5 (1)

Table 5. *Close intermolecular contacts* (Å)

Orange G/Adenine		Orange G/Cytosine	
O(1)···N(4)	2.742 (4)	O(1)···O(8W)	2.920 (2)
O(2)···N(3)	2.809 (4)	O(2)···N(6)	2.857 (2)
O(3)···O(12Wⁱ)	2.850 (5)	O(3)···N(7)	2.740 (2)
O(3)···O(10Wⁱ)	2.988 (5)	O(4)···N(6ⁱᵛ)	2.803 (2)
O(4)···O(12Wⁱ)	2.778 (5)	O(5)···N(4ᵛⁱⁱ)	2.971 (2)
O(5)···N(3ⁱⁱ)	2.824 (5)	O(6)···N(3)	2.837 (2)
O(6)···O(10W)	2.774 (4)	O(7)···N(5ᵛⁱⁱⁱ)	2.740 (2)
O(7)···O(11Wⁱⁱⁱ)	2.928 (4)	O(8W)···N(8ⁱˣ)	2.761 (2)
O(8W)···N(6)	2.873 (4)	O(8W)···O(9ⁱˣ)	2.873 (2)
O(9W)···N(11)	2.760 (5)	O(10)···N(4)	2.699 (2)
O(9W)···N(5ᵛ)	2.878 (5)	O(10)···N(3)	2.915 (3)
O(10W)···N(8)	2.855 (4)		
O(11W)···O(12Wᵛ)	2.635 (7)		
O(11W)···N(9)	2.694 (4)		
N(8)···N(12ᵛⁱ)	2.882 (5)		

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, 1 + y, z$; (iii) $-x, 1 - y, -z$; (iv) $-1 + x, -1 + y, z$; (v) $x, -1 + y, z$; (vi) $-1 - x, 1 - y, 1 - z$; (vii) $-x, 2 - y, 2 - z$; (viii) $1 + x, y, -1 + z$; (ix) $1 - x, 3 - y, 2 - z$.

In both structures, H atoms bonded to C atoms were placed in calculated positions and were not refined. H atoms bonded to N atoms in Orange G/adenine were located in difference maps and their positional parameters were refined. Peaks were also found near the water O atoms, but their positions were not considered chemically reasonable and were left unassigned. H atoms bonded to N atoms and to the water O atom in Orange G/cytosine were located and their positional parameters were refined. Refinement of a secondary extinction coefficient (Zachariasen, 1963) was considered warranted only in the case of Orange G/cytosine. Data collection and cell determination were carried out using Enraf–Nonius CAD-4 software. Data reduction and structure refinement used the *TEXSAN* software package (Molecular Structure Corporation, 1985). Structure solution was accomplished using *SHELXS*86 (Sheldrick, 1985). Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

References

Conroy, M. J. & Lovrien, R. E. (1992). *J. Cryst. Growth*, **122**, 213–222.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Ojala, W. H., Lu, L. K., Albers, K. E., Gleason, W. B., Richardson, T. I., Lovrien, R. E. & Sudbeck, E. A. (1994). *Acta Cryst.* B50. In the press.

Olivieri, A. C., Wilson, R. B., Paul, I. C. & Curtin, D. Y. (1989). *J. Am. Chem. Soc.* **111**, 5525–5532.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Weaver, J. L., Pine, P. S., Anand, R., Bell, S. & Aszalos, A. (1992). *Antivir. Chem. Chemother.* **3**, 147–151.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Sorbic Acid

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## Abstract

The crystal and molecular structure of sorbic acid [(E,E)-2,4-hexadienoic acid], $C_6H_8O_2$, has been determined. There appears to be no delocalization of the C_{sp^2}—C_{sp^2} bonds, arranged in an E,E configuration, which have lengths of 1.328 (2) and 1.335 (2) Å (double) and 1.442 (2)–1.487 (2) Å (single). Dimers are formed in the crystal with an intermolecular O···O separation of 2.632 (2) Å; O—H 0.99 (2), H···O 1.65 (2) Å, O—H···O 174 (2)°.

Comment

Sorbic acid, (I), exhibits antibacterial and antifungal properties (Martindale, 1993) and has been used to prevent spoilage of syrup by moulds (Richards, 1972). The structures of numerous simple carboxylic acids have been determined and many involve intermolecular hydrogen bonding (Speakman, 1972; CSSR, 1993). It is difficult to obtain well formed crystals of sorbic acid and attempts to determine the cell dimensions by X-ray powder diffraction from a commercial crystalline sample (99 + %, Sigma) were unsuccessful. After repeated crystallizations from ethanol only one specimen was considered suitable for data collection.

(I)
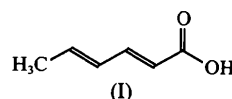
The study shows that dimers form in the crystal with intermolecular hydrogen bonding around a centre of symmetry. The short O···O separation is