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The Crystal Structure of the *p*-Bromophenylhydrazone of Monomeric Dehydroascorbic Acid

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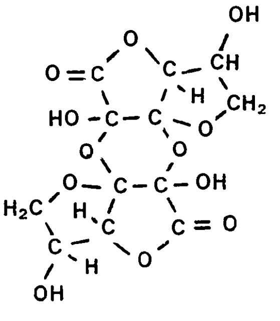
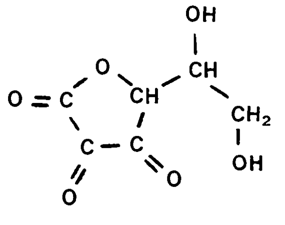
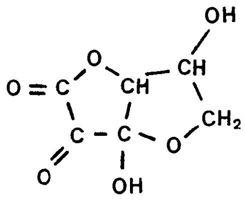
The crystal structure of $C_{12}H_{11}O_5N_2Br$ has been determined by X-ray diffraction with an automatic diffractometer and Mo $K\alpha$ radiation. The space group is $P2_12_12_1$ with $a = 18·020$ (3), $b = 12·859$ (1), $c = 5·754$ (1) Å. The parameters were refined to $R = 0·042$ and $R_w = 0·025$ for 1142 reflexions. The average standard deviations are 0·008 Å and 0·6° for non-hydrogen atoms. In contrast to the structure of the crystalline dimer, this molecule has an open side chain, and the lactone ring has a hydrazone group attached to C(2). The latter moiety is planar with sp^2 hybridization at the nitrogen and neighbouring atoms. The open side chain is caused by π-electron delocalization, and sp^2 hybridization at C(3) of the dehydroascorbic acid molecule. The bond distances are normal, except for those involved in the resonance system. The hydrogen bonds extend only along **c**, except for an intramolecular bond between a nitrogen atom in the hydrazine group and carbonyl in the lactone group.

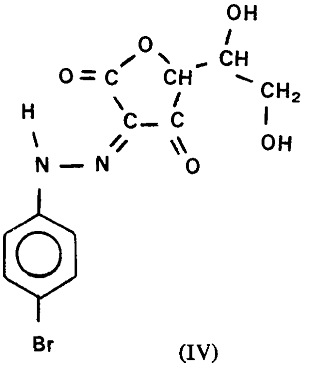
Introduction

Crystalline dehydroascorbic acid has as yet been isolated only in its dimeric form, and shown to comprise a five-membered ring system (I) (Hvoslef, 1972*a*). Difficulties in preparing the monomer in a pure crystalline form have led to a long debate about its structural formula. The traditional formula (II) is not compatible with its ultraviolet spectrum and the colourless nature of the compound. An alternative formula (III) has been suggested (Hvoslef, 1972*b*) on the basis of the crystal structure of the dimer and on the properties of the n.m.r. spectra in non-aqueous solutions. The present paper deals with the structure of a *p*-bromophenylhydrazine derivative (IV) of this oxidation product of vitamin C. For a compound with the hypothetical structure (III), however, the reaction with *p*-bromophenylhydrazine might be expected to lead to the opening of the furanoid ring, and this is actually shown to be the case in our work. In solution, an equilibrium between (II) and (III) is conceivable, and conversion of (II) into (III) may simply be thought of as an intramolecular nucleophilic addition. The relative stabilities of these compounds are apparently in favour of (III), according to our n.m.r. spectra.


(I)


(II)


(III)


(IV)

Experimental

A mixture of pure dehydro-L-(+)-ascorbic acid dimer and *p*-bromophenylhydrazine in dimethylacetamide was allowed to stand overnight at room temperature. Addition of water produced a syrupy, yellowish precipitate which on recrystallization from absolute alcohol gave thin, yellow needles (m.p. 208 °C). The crystals were small and generally of low quality, but a crystal with satisfactory optical properties was obtained by cutting a relatively large specimen. This fragment was prismatic with the dimensions 0·012 × 0·005 × 0·003 cm. Weissenberg diagrams identified the space group as $P2_12_12_1$ from systematic absences. X-ray data were obtained on an automatic Picker diffractometer operating in the ω–2θ mode. With Mo $K\alpha$ radiation (λ = 0·7107 Å) and a limiting 2θ of 65°, 2668 reflexions were considered. Because of the weak intensities of the reflexions at higher 2θ values, only those with $2\theta < 50{\cdot}5°$ were used in the analysis (1142). The scan speed was 1° min^{-1}, and the background counts lasted for 30 s on each side of the Bragg peak. The stability of the crystal was checked by three test reflexions, but no disintegration was observed. Our data were corrected for absorption and converted to structure amplitudes by programs adapted for CDC 3300 by Dahl, Gram, Groth, Klewe & Rømming (1970).

Unit cell and space group

$C_{12}H_{11}O_5N_2Br$, $M = 343{\cdot}141$, $a = 18{\cdot}020\,(3)$, $b = 12{\cdot}859\,(1)$, $c = 5{\cdot}754\,(1)$ Å; $V = 1333{\cdot}3$ Å^3. Space group $P2_12_12_1$, $Z = 4$, d(obs) = 1·68, d(calc) = 1·709 g cm^{-3}, μ(Mo $K\alpha$) = 32·6 cm^{-1}.

Structure determination

The structure was solved by the heavy-atom method. The position of the Br atom was found from Harker sections, and the resulting phases were used to calculate Fourier syntheses which gave adequate information about most of the light atoms. Least-squares refinements were performed on CYBER 74 with pro-

Table 1. *Fractional coordinates for the atoms in the p-bromophenylhydrazone of dehydroascorbic acid*

Standard deviations are in parentheses. The values are multiplied by 10^4 for the heavy atoms and by 10^3 for H atoms. The latter are identified by the atoms to which they are attached.

	x	y	z
Br	−517 (0)	5827 (1)	15579 (1)
N(2)	1393 (2)	4200 (5)	7723 (9)
N(1)	1395 (3)	3217 (4)	7132 (11)
C(12)	917 (3)	5606 (4)	10026 (12)
C(11)	477 (4)	5980 (5)	11795 (12)
C(10)	99 (3)	5312 (5)	13201 (12)
C(9)	147 (3)	4252 (6)	12843 (12)
C(8)	574 (4)	3873 (4)	11048 (12)
C(7)	958 (3)	4542 (4)	9625 (13)
C(6)	3612 (4)	1459 (5)	730 (15)
C(5)	3110 (4)	1422 (5)	2847 (13)
C(4)	2369 (4)	1950 (5)	2407 (11)
C(3)	1860 (3)	1905 (5)	4486 (14)
C(2)	1791 (3)	2952 (5)	5311 (12)
C(1)	2197 (3)	3640 (6)	3749 (12)
O(6)	3292 (3)	953 (4)	−1183 (9)
O(5)	3486 (3)	1930 (4)	4682 (8)
O(4)	2497 (2)	3060 (3)	2001 (7)
O(3)	1602 (2)	1092 (3)	5270 (8)
O(1)	2279 (2)	4568 (3)	3859 (9)
N(2)H	171 (4)	468 (5)	680 (12)
C(4)H	216 (3)	161 (4)	95 (10)
C(5)H	296 (3)	67 (5)	320 (9)
C(6)H1	414 (3)	124 (4)	115 (10)
C(6)H2	370 (3)	214 (4)	23 (11)
C(8)H	64 (3)	319 (4)	1083 (11)
C(9)H	−10 (3)	387 (4)	1378 (10)
C(11)H	42 (3)	670 (4)	1204 (10)
C(12)H	114 (3)	606 (4)	906 (11)
O(6)H	326 (4)	48 (5)	−89 (15)
O(5)H	342 (5)	162 (5)	564 (13)

Table 2. *Thermal parameters for the atoms in the p-bromophenylhydrazone of dehydroascorbic acid*

Standard deviations are in parentheses. Temperature factors are in the form $T = \exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$, and the values are multiplied by 10^4. For the H atoms the isotropic values are given, and * indicates a fixed value.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	30 (0)	59 (0)	253 (2)	16 (1)	54 (3)	−41 (2)
N(2)	17 (2)	41 (4)	215 (20)	1 (5)	8 (10)	−18 (20)
N(1)	23 (2)	29 (4)	229 (23)	−5 (5)	14 (13)	−17 (18)
C(12)	26 (2)	30 (5)	285 (38)	−5 (5)	−3 (14)	32 (19)
C(11)	24 (2)	40 (5)	348 (28)	9 (8)	35 (18)	−61 (23)
C(10)	18 (2)	46 (5)	269 (29)	7 (6)	9 (14)	0 (21)
C(9)	20 (2)	49 (6)	222 (27)	−4 (6)	34 (13)	26 (24)
C(8)	20 (2)	35 (5)	247 (28)	−6 (7)	12 (16)	−18 (19)
C(7)	15 (2)	37 (4)	192 (23)	5 (5)	15 (13)	−2 (19)
C(6)	24 (3)	50 (5)	216 (29)	−11 (6)	6 (19)	33 (25)
C(5)	20 (2)	46 (5)	142 (25)	1 (6)	27 (14)	−2 (20)
C(4)	24 (3)	40 (5)	121 (25)	−11 (6)	22 (14)	−20 (20)
C(3)	21 (2)	42 (5)	174 (25)	−2 (6)	19 (15)	2 (24)
C(2)	20 (2)	36 (5)	155 (28)	0 (5)	8 (14)	0 (20)
C(1)	17 (2)	51 (5)	130 (29)	−3 (6)	−15 (13)	−5 (22)
O(6)	44 (2)	46 (4)	130 (19)	5 (6)	9 (9)	11 (16)
O(5)	35 (2)	57 (4)	159 (19)	−11 (5)	−32 (12)	−6 (14)
O(4)	26 (2)	43 (3)	186 (16)	3 (4)	38 (9)	62 (14)
O(3)	36 (2)	38 (3)	317 (21)	−21 (4)	84 (11)	−23 (15)
O(1)	31 (2)	36 (3)	284 (22)	−13 (4)	28 (10)	29 (14)

Table 2 (*cont.*)

	B_{iso}		B_{iso}
N(2)H	7·2 (2·3)	C(9)H	3·0 (*)
C(4)H	3·0 (*)	C(11)H	3·0 (*)
C(5)H	3·0 (*)	C(12)H	3·0 (*)
C(6)H1	2·8 (1·4)	O(6)H	4·0 (*)
C(6)H2	2·3 (1·4)	O(5)H	4·0 (*)
C(8)H	3·0 (*)		

grams adapted by Groth (1973). With isotropic thermal parameters the conventional R index terminated at 0·15. An anomalous scattering amplitude was introduced for Br (Cromer & Waber, 1965; Cromer, 1965) and adapted to the known absolute configuration of the molecule. The form factors for C, O and N were from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). Subsequent full-matrix least-squares refinements including anisotropic thermal parameters for the heavy atoms resulted in $R = 0{\cdot}042$ and $R_w = 0{\cdot}025$, respectively.

The analysis of extinction effects for this crystal gave the value $C = 1{\cdot}0 \times 10^{-6}$ in the Zachariasen (1963) formula. A correction, however small, was performed on our data, and the final difference electron density map showed no residual above 0·4 e Å^{-3}.

Atomic coordinates are in Table 1 and the thermal parameters in Table 2.*

Discussion

A stereo view of the structure is shown in Fig. 1. It reveals a molecule with an open side chain, and details are shown in the *ORTEP* plot of Fig. 2. The interatomic distances and angles for the heavy atoms are included in the drawing. The average standard deviations are $\bar{\sigma} = 0{\cdot}008$ Å and 0·6° for these bonds, except

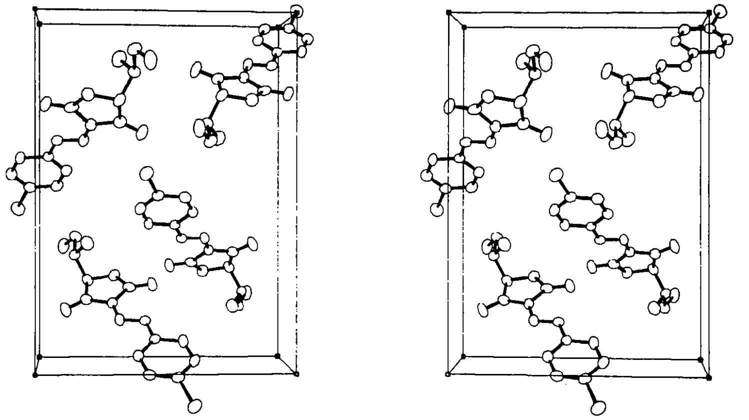


Fig. 1. Stereo view of the crystal structure of the *p*-bromophenylhydrazone of dehydroascorbic acid. The view is along −**c** with **b** to the right and **a** upwards. This left-handed system conforms with the absolute configurations of the molecule.

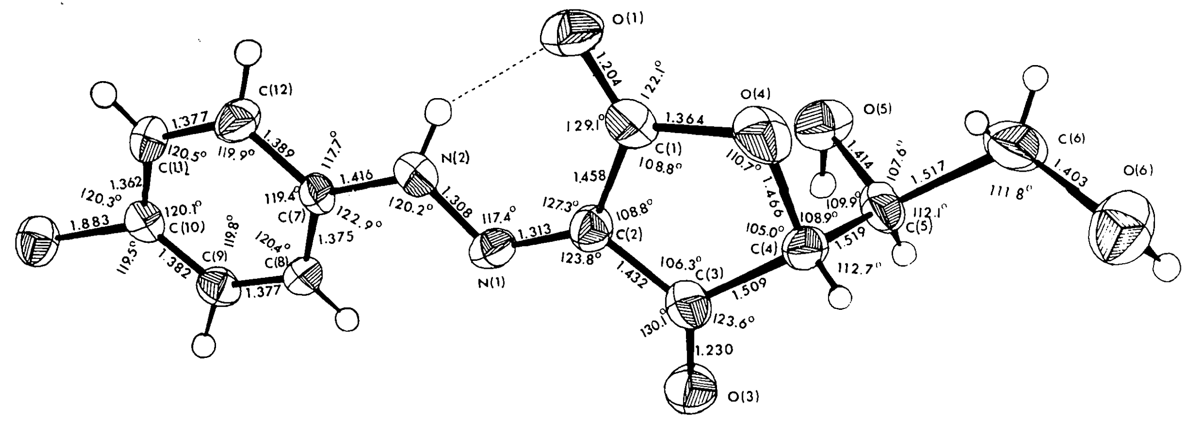


Fig. 2. *ORTEP* plot (Johnson, 1965) of the *p*-bromophenylhydrazone of dehydrascorbic acid with thermal ellipsoids at 50% probability. Distances (Å) and angles (°) for non-hydrogen atoms are included in the drawing. Average standard deviations are 0·008 Å and 0·6° (0·006 Å for C–Br). The intramolecular hydrogen bond is represented by a dashed line.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31204 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Br–C(10) where the value is 0·006 Å. For bonds and angles involving H atoms the corresponding values are 0·06 Å and 3·9°.

Table 3. *Distances* (Å) *from planes through parts of the title compound*

An asterisk indicates atoms used to define the planes. C(5) is included to show the direction of the deviation.

C(7)*	0·009 Å	Hydrazine group	O(1)*	0·002 Å	
N(2)*	−0·012		C(1)*	0·006	
N(1)*	−0·005		C(2)*	−0·018	
C(2)*	0·015		N(1)*	0·017	
C(3)*	−0·004		N(2)*	−0·009	
O(3)	−0·071		N(2)H	−0·095	
C(4)	0·007				
C(5)	−1·296				
C(7)*	0·006	Phenyl ring	O(4)*	0·000	Lactone group
C(8)*	0·003		C(1)*	0·000	
C(9)*	−0·006		O(1)*	0·000	
C(10)*	0·001		C(2)*	0·000	
C(11)*	0·007		C(3)	−0·024	
C(12)*	−0·011		O(3)	−0·021	
Br	0·063		C(4)	−0·126	
N(2)	0·044		C(5)	−1·460	
N(1)	0·189				

Table 4. *Selected conformational angles in the p-bromophenylhydrazone of dehydroascorbic acid*

Conformational angle *A*(1)–*A*(2)–*A*(3)–*A*(4) is viewed down the *A*(2)–*A*(3) bond with a clockwise angle of *A*(1) to *A*(2) taken to be positive.

Hydrazine moiety	
O(3)–C(3)–C(2)–N(1)	−1·8°
C(3)–C(2)–N(1)–N(2)	+178·5
C(2)–N(1)–N(2)–C(7)	+178·0
N(1)–N(2)–C(7)–C(8)	+5·8
O(1)–C(1)–C(2)–N(1)	+3·7
C(1)–C(2)–N(1)–N(2)	−4·5
Side chain	
O(6)–C(6)–C(5)–O(5)	+178·8
O(5)–C(5)–C(4)–C(3)	−61·5
O(5)–C(5)–C(4)–O(4)	+54·6
C(6)–C(5)–C(4)–O(4)	−64·8
C(6)–C(5)–C(4)–C(3)	+179·2

Molecular geometry

The most striking feature of this molecule is the geometry of the hydrazine moiety and its close neighbours. C(7), N(2), N(1), C(2), C(3) and C(4) form an almost planar, extended zigzag chain with bond angles typical of sp^2 hybridization, except for C(4). Moreover, O(1), C(1), C(2), N(1), N(2) and N(2)H constitute a nearly planar ring involving a relatively strong intramolecular hydrogen bond. Deviations of the atoms from the best planes through these systems are given in Table 3, and some relevant dihedral angles in Table 4.

The lactone ring is relatively flat, although C(4) deviates by 0·126 Å from a plane defined by the coplanar C(1), C(2), O(1) and O(4) atoms. The deviation is *endo* with respect to C(5), and this is also the case for the C(3)–O(3) group, although the deviation for this group is hardly significant.

The side chain of the sugar is very nearly staggered, with O(5) and O(6) *anti.*

The inclination of the planar phenyl ring to the rest of the molecule is described by the conformational angles and roughly amounts to an anti-clockwise twist of about 5° of the phenyl ring relative to the lactone ring when seen from the sugar moiety.

Bond distances

In the phenyl ring the bond lengths vary between 1·362 and 1·389 Å with a mean of 1·377 Å which is not significantly different from the expected value of 1·39 Å. The C angles are 120° within their standard deviations. The substituted Br and N(2) atoms, however, deviate significantly from the least-squares plane through the C atoms in the phenyl ring (Table 3).

The bond distances of the atoms in the hydrazine moiety are noteworthy as they differ from those previously reported, of which, to our knowledge, the *p*-bromophenylhydrazone of mannose (Furberg & Solbakk, 1969) is the most accurate. Some relevant bond lengths compare as follows (the title compound mentioned first): C(7)–N(2) 1·416, 1·373 Å; N(2)–N(1) 1·308, 1·370 Å; N(1)–C(2) 1·313, 1·254 Å; C(2)–C(3)

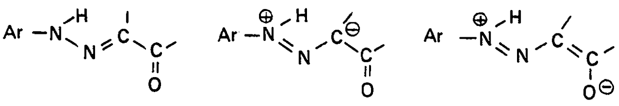
Table 5. *Distances* (Å) *and angles* (°) *involving* H *atoms*

Average standard deviations are 0·06 Å and 3·9° for bonds involving hydrogen atoms and 0·006 Å for donor–acceptor distances. The H atoms are identified by the atom to which they are attached.

A–H···*B*	Symmetry code for *B*	*A*–H	H···*B*	*A*···*B*	*A*–H···*B*	*C*–*A*–H
N(2)–H···O(1)	$x, \; y, \; z$	0·99 Å	1·987 Å	2·778 Å	135°	123°
O(5)–H···O(6)	$x, \; y, \; z+1$	0·69	2·030	2·713	168	104
O(6)–H···O(3)	$\frac{1}{2}-x, \; -y, \; z-\frac{1}{2}$	0·63	2·147	2·767	168	106

C(7)—C(8)—C(8)H	118°	C(3)—C(4)—C(4)H	115°	C(4)—H	1·01 Å
C(9)—C(8)—C(8)H	122	O(4)—C(4)—C(4)H	110	C(5)—H	1·02
C(8)—C(9)—C(9)H	124	C(5)—C(4)—C(4)H	106	C(6)—H1	1·03
C(10)—C(9)—C(9)H	116	C(4)—C(5)—C(5)H	103	C(6)—H2	0·94
C(10)—C(11)—C(11)H	119	O(5)—C(5)—C(5)H	115	C(8)—H	0·89
C(12)—C(11)—C(11)H	121	C(6)—C(5)—C(5)H	110	C(9)—H	0·86
C(11)—C(12)—C(12)H	119	C(5)—C(6)—C(6)H1	111	C(11)-H	0·94
C(7)—C(12)—C(12)H	121	O(6)—C(6)—C(6)H1	116	C(12)-H	0·90
		C(5)—C(6)—C(6)H2	112		
		O(6)—C(6)—C(6)H2	105		
		H1—C(6)—H2	99		

1·432, 1·504 Å. Although the values of σ preclude significance for these differences, the lengths indicate considerable π electron delocalization in the system mentioned above. The resonance structures which give the major contribution are presumably



and they are apparently energetically preferred to a fused-ring system indicated by (III). We therefore conclude that if a two-ring system of dehydroascorbic acid really is the 'normal' species, it will be disrupted upon formation of a hydrazone derivative. In order to keep a double ring intact, substituents at C(2) are required which do not lead to delocalization of the π electrons or to sp^2 hybridization at C(3). This is presumably the case for the normal hydrate of the monomer and for the so-called 'methanol complex'. These compounds are difficult to crystallize properly, as is indeed the case for the pure monomer. We have, however, determined the crystal structure of a double ring derivate of ascorbic acid where the substituents at C(2) are OH and benzyl (to be published shortly).

The residual C–C and C–O bonds are normal, and compare well with those generally observed for carbohydrates.

Hydrogen bonding

Whereas the N(2)–H···O(1) bond is intramolecular and tends to stabilize the planar hydrazine group, the O(6)–H···O(3) and O(5)–H···O(6) bonds combine to respectively form and reinforce a helical interaction which runs along **c**. Participants are only neighbouring ascorbate moieties that are arranged head-to-head across screw axes. This leads to piles of symmetry-related molecules which have no obvious interaction with other piles, except for van der Waals forces. Table 5 lists all bond lengths and angles involving H atoms.

Thermal analysis

Neither the whole molecule nor parts of it could be satisfactorily correlated to a rigid-body model by the procedure given by Schomaker & Trueblood (1968). The thermal amplitudes are, however, moderate and it is unlikely that these could affect the bond lengths and angles given in Fig. 2.

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Bis-(2-picolyl-phenylketonato)kupfer(II)

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$Cu(C_{13}H_{10}NO)_2$, monoclinic, $P2_1/n$, $a=9{\cdot}55$ (1), $b=22{\cdot}40$ (2), $c=10{\cdot}01$ (1) Å, $\beta=97{\cdot}8$ (2)°, $Z=4$, $D_c=1{\cdot}42$, $D_x=1{\cdot}41$ g cm^{-3}, $M=456$, $F(000)=744$, $\mu=27$ cm^{-1} (Co $K\alpha$). 1720 intensities have been collected from Weissenberg photographs *hk*0–*hk*6 and *h*0*l* taken with Co $K\alpha$ radiation. The structure has been solved by the heavy-atom technique and refined by block-diagonal least-squares calculations to $R=0{\cdot}12$.

Einleitung

Kupfer bildet mit Picolylketonen Bis-Chelate unter Ausbildung eines koordinativen Sechsringes. Als Ligatoratome fungieren die Stickstoff- und Sauerstoffatome. Strukturell ähnlich sind die Bis-Chelate des Kupfers mit N-substituierten Salicylaldiminen und *o*-Hydroxyacetophenoniminen aufgebaut. Anderseits zeigen die