

Molecular Orbital Studies of L-Ascorbic Acid and Some Related Molecules

EVEN FLOOD* and P. N. SKANCKE*

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

In this work the structure and UV spectrum of L-ascorbic acid and ascorbate anion are examined through semiempirical calculations. A scheme for π -electron calculations previously described is extended to include methylene, using 1,3-cyclopentadiene as a reference system. The methylene parameters are used in calculations on α -hydroxytetronic acid and α -hydroxytetronate, which in the π -electron system are similar to ascorbic acid and ascorbate. The results for the UV absorption bands are close to the experimental values, the bond lengths are not so well reproduced.

The crystal and molecular structure of L-ascorbic acid (I) and ascorbate anion (II) have been determined by X-ray and neutron diffraction.¹⁻³ These structures display several interesting features; particularly, in the acid, the carbon-oxygen bond lengths in the two hydroxyl groups are found to be significantly different from each other. One of the purposes of this study is to investigate these structures using semiempirical LCAO-MO-SCF methods.

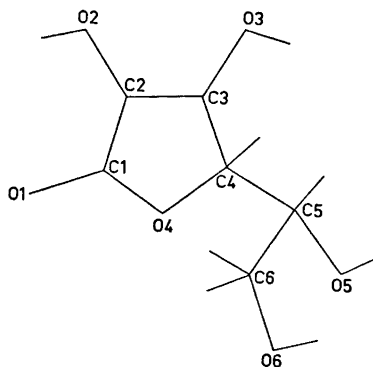


Fig. 1. Ascorbic acid with labelling of atoms.

* Present address: University of Tromsø, N-9000 Tromsø, Norway.

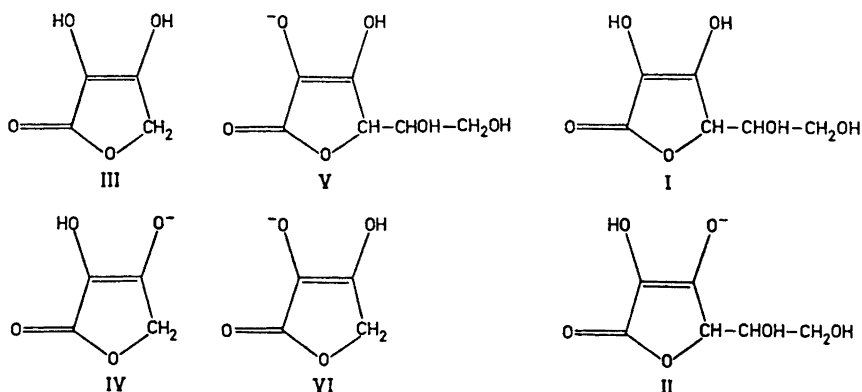


Fig. 2. Structure of molecules examined. I L-Ascorbic acid. II Ascorbate anion. III α -Hydroxytetronic acid. IV α -Hydroxytetronate anion.

Most of the calculations were confined to a study of the π -electrons in the ring, using the ZDO approximation. One problem that arose in this connection was to determine the effect on the electronic structure of the ring when the chain $-\text{CHOH}-\text{CH}_2\text{OH}$ was substituted by a hydrogen atom. This effect was studied using the CNDO/2 method on the molecules with and without chain.⁴⁻⁶ The latter systems are α -hydroxytetronic acid (III) and α -hydroxytetronate anion (IV). The π -electron calculations were made on these two molecules.

We also wanted to include the hyperconjugation from the methylene group to the π -electrons. In order to do that, we had to extend the π -electron calculations to include parameters for methylene.

When ascorbic acid is protolyzed to ascorbate anion, this can occur in two ways, giving two different ions. Chemical evidence indicates that only one kind is formed. As a part of this work, π -electron calculations were made to find out if this can be explained from the π -electron energy differences alone.

For both (I) and (II), experimental UV-data exist. The first transition has been interpreted as a $\pi \rightarrow \pi^*$ transition in both molecules. Another purpose of this work is to calculate these transition energies. The validity of these predictions may give an indication of the extent to which the method can yield quantitatively satisfactory results in cases with several hetero atoms.

PARAMETERS FOR THE π -ELECTRON CALCULATIONS

The π -electron calculations were made using a scheme for the semi-empirical parameters proposed for unsaturated hydrocarbons.⁷ The scheme has later been extended to include the carbonyl group,⁸ ether oxygen,⁹ and other heteroatoms as well as hyperconjugation from the methyl group.¹⁰ For the molecules (III) and (IV) we wanted to include the hyperconjugation from the methylene group. This was done by a method similar to the one used for methyl.¹⁰

As the parametrization scheme has been described in the papers already referred to, only a brief outline will be given here. The main characteristic is that the one-electron parameter W_μ is made dependent on the surroundings of the atom μ . This dependence is expressed by

$$W_\mu = W_\mu^\circ + \sum_\nu \Delta W(\nu) \quad (1)$$

where the sum is over nearest neighbours. $\Delta W_\mu(\nu)$ varies with the nature of the neighboring atom ν , and, for some bonds, with the bond length $R_{\mu\nu}$ through the assumed linear relation

$$\Delta W_\mu(\nu) = \Delta W_\mu^\circ(\nu) + \delta W(R_{\mu\nu} - R_{\mu\nu}^\circ) \quad (2)$$

Similarly the two-center parameters $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ are made dependent of the bond length through the relations

$$\beta_{\mu\nu} = \beta_{\mu\nu}^\circ + \delta\beta(R_{\mu\nu} - R_{\mu\nu}^\circ) \quad (3)$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^\circ + \delta\gamma(R_{\mu\nu} - R_{\mu\nu}^\circ) \quad (4)$$

The parameters are chosen to fit the UV-spectra and ionisation potentials (using Koopmans' theorem) of several reference molecules.

In addition to the parameters previously determined, we need for this investigation parameters for the methylene group, for the carbon-methylene bond, and for the oxygen-methylene bond. For the methylene group and the carbon-methylene bond, a procedure much similar to the one proposed for methyl¹⁰ is followed.

The methylene group may be described by two $1s$ orbitals from the two hydrogen atoms located symmetrically about the molecular plane chosen as the xy -plane, one $2pz$ orbital from carbon, and one sp^2 orbital symmetrical about the xy -plane. As the group has four electrons, these atomic orbitals (AO's) can be combined to form two doubly occupied quasi AO's:

$$\sigma = c(sp^2) + d(s_1 + s_2) \quad (5)$$

$$\pi = a(pz) + b(s_1 - s_2) \quad (6)$$

where a , b , c , and d are constants. Of these, the first has σ -symmetry and the second has π -symmetry. We see that with this description, methylene can be formally treated as a lone pair. In order to calculate $\gamma_{\mu\nu}$ from methylene to a non-neighboring atom using the ball-approximation,¹¹ we had to approximate this π -orbital with two uniformly charged spheres touching each other somewhere on the line from carbon to the line connecting the hydrogen atoms.

The parameters $\gamma_{C\pi}$ and $\beta_{C\pi}$ were assumed independent of $R_{C\pi}$, and ΔW_μ (C) was included in W_π so the parameter determined was the total W_π , not W_π° . Thus, the following five parameters had to be determined: $\beta_{C\pi}$, $\gamma_{C\pi}$, $\nabla W_C(\pi)$, W_π and the one-center parameter $\gamma_{\pi\pi}$.

The simplest approach to the problem, is to place the ball center in the middle of the carbon-hydrogen axis, and use the parameters for methyl, following the reasonable chemical argument that the effects from methyl and methylene must be similar. This approach has been tried giving good results¹² (see also Table 2). In the present paper the parameters were obtained from

calculations on 1,3-cyclopentadiene using experimental electronic transition energies and ionisation potentials as reference values.

The electronic transitions of cyclopentadiene have been studied both experimentally¹³⁻¹⁵ and theoretically.¹⁶ In the theoretical study referred to, a modified CNDO method with configuration interaction was used. The results obtained indicate that of the four lowest electronic transitions, one band at 7.4 eV represents a $\sigma \rightarrow \pi^*$ transition, while the other three bands at 5.34, 6.2, and 7.9 eV correspond to $\pi \rightarrow \pi^*$ transitions. Our calculations seem to confirm this, as the value 7.4 eV is very difficult to reproduce as a $\pi \rightarrow \pi^*$ transition.

CNDO/2 calculations on cyclopentadiene showed that for the occupied orbitals the coefficients for the p_z orbital are larger than for $(s_1 - s_2)$. This led us to place the ball center somewhat closer to the carbon atom than to the hydrogen-hydrogen axis. We chose the distance 0.26 Å from the former, and 0.35 Å from the latter.

The parameter $\gamma_{\pi\pi}$ was difficult to determine using the spectral values as reference. Predicted UV-spectral values and ionisation potential are very insensitive to changes in this parameter. Accordingly, a precise value of this parameter is not important in the present context. To obtain a value we normalized the π -orbital given by (6), assuming $a/b = 5/4$ for the reason men-

Table 1. Parameters for methylene, compared with parameters for methyl.¹⁰ Ball radius in Å and integrals in eV.

$\gamma_{\text{CH}_2-\text{CH}_2}$	10.01	$\gamma_{\text{CH}_2-\text{CH}_2}$	7.42
W_{CH_2}	-12.0	W_{CH_2}	-13.38
$\Delta W_{\text{C}}(\text{CH}_2)$	0.50	$\Delta W_{\text{C}}(\text{CH}_2)$	0.636
$\beta_{\text{C}-\text{CH}_2}$	-1.38	$\beta_{\text{C}-\text{CH}_2}$	-1.07
$\gamma_{\text{C}-\text{CH}_2}$	5.70	$\gamma_{\text{C}-\text{CH}_2}$	5.70
Ball radius	1.76	Ball radius	2.40
		$\gamma_{\text{O}-\text{CH}_2}$	7.00
		$\beta_{\text{O}-\text{CH}_2}$	-1.25
		$\Delta W_{\text{CH}_2}(\text{O})$	-0.16
		$\Delta W_{\text{O}}(\text{CH}_2)$	1.51

Table 2. Semiempirical calculations on 1-3 cyclopentadiene. All values in eV.

	Exp. values	CNDO	PPP ^a	PPP ^b	PPP ^c
Ionisation potential	-8.58 ^d		-8.60	-8.60	-8.58
Transition energies	5.34	4.8	5.51	5.51	5.36
	6.2	6.3	6.4	6.4	6.5
	7.9	7.9	7.8	7.8	7.9

^a Parameters for methyl used for methylene. ^b Same as above, but with $\gamma_{\pi\pi} = 7.42$. ^c Methylene parameters developed in this work. ^d Ref. 17.

tioned above. We then decomposed the integral as a sum of integrals over $2pz$, s_1 , and s_2 . Three-center integrals were omitted, and the one- and two-center integrals were estimated from correlation corrected values for $(pzpz|pzpz)$ and $(ss|ss)$. By this method, we arrived at the value 7.42 eV. As seen in Table 2, the change from 10.01 eV for methyl has very little effect. The remaining four parameters were determined so as to give the best fit to the experimental values. The results are given in Tables 1 and 2.

The method used to estimate the parameters $\gamma_{O\pi}$, $\beta_{O\pi}$, $\Delta W_O(\pi)$ and $\Delta W_\pi(O)$ are as follows:

The ΔW values were assumed to be the same as for the C–O and C–C groups. As the W_π determined for methylene is the total value, we estimated an effective $\Delta W_\pi(O)$ from the formula

$$W_\pi(O,C) = W_\pi(C,C) - \Delta W_\pi(C) + \Delta W_\pi(O) = W_\pi(C,C) - \Delta W_C(C) + \Delta W_C(O) \quad (7)$$

where the last two terms give the effective $\Delta W_\pi(O)$ used in the calculation. The value of $\beta_{O\pi}$ was obtained from the relation

$$\beta_{CO}/\beta_{CC} = \beta_{\pi O}/\pi C \quad (8)$$

where all the β -values were taken at the same bond length, 1.50 Å found through the linear relation (3).

Table 3. π -Electron parameters used in the calculations.

Carbon-carbon		Carbon-ether oxygen		Carbonyl	
γ_{CC}	11.97 eV	γ_{OO}	18.89 eV	γ_{OO}	18.89 eV
γ_{C-C}^o	6.91 eV	γ_{CO}	6.20 eV	γ_{CO}	9.33 eV
$\delta\gamma_{CC}$	-3.99 eV/Å				
β_{CC}	-2.42 eV	β_{CO}	-1.80 eV	β_{CO}	-2.46 eV
$\delta\beta_{CC}$	3.05 eV/Å				
W_C	-9.84 eV	W_O	-11.18 eV	W_O	-19.60 eV
$\Delta W_C(C)$	0.07 eV	$\Delta W_C(O)$	-0.09 eV	$\Delta W_C(O)$	-0.71 eV
δW_{CC}	9.22 eV/Å	$\Delta W_O(C)$	1.51 eV	$\Delta W_O(C)$	1.30 eV
Ball radius	1.47 Å		1.09 Å		1.09 Å
R_{CC}^o	1.395 Å	R_{C-O}	1.35 Å	R_{C-O}	1.22 Å

The value of $\gamma_{O\pi}$ was interpolated from a curve with the constraints that for $R_{O\pi}=0$, $\gamma_{O\pi}=\frac{1}{2}(\gamma_{OO}+\gamma_{\pi\pi})$ and for $R_{O\pi}=4$ Å, $\gamma_{O\pi}$ was equal to the theoretical value for γ_{OC} . Interpolation for the value $R_{O\pi}=1.62$ Å gave the value 7.00 eV.

RESULTS AND DISCUSSION

The structure of L-ascorbic acid and ascorbate anion have been examined by Hvoslef.¹⁻³ This structure was used as input in the CNDO/2 calculations on the molecules (I) and (II). In (III) and (IV), the ring structures of the first two were used, but the ring was assumed planar and the methylene group was

assumed to be symmetrical about the molecular plane. As the ring is not exactly planar, this assumption introduced some small changes in the oxygen-methylene bond.

The premise for the π -electron calculations is that the electronic structure of the ring is not much changed when the chain $-\text{CHOH}-\text{CH}_2\text{OH}$ is substituted by hydrogen. To test this assumption, CNDO/2 calculations on all four molecules were made, and the charges on the nuclei were compared. The results of this calculation, shown in Table 4, show that the variations are small.

Table 4. CNDO/2 results for charge distributions.

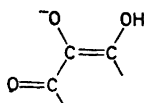
	(I)	(II)	(III)	(IV)
O(4)	6.2414	6.3032	6.2333	6.2774
C(1)	3.6213	3.6356	3.6220	3.6356
O(1)	6.3224	6.4459	6.3176	6.4193
C(2)	3.9961	4.1515	3.9900	4.1561
O(2)	6.2453	6.2924	6.2437	6.2322
C(3)	3.8446	3.7911	3.8421	3.7949
O(3)	6.2341	6.4959	6.2326	6.4999
C(4)	3.8848	3.9018	3.8858	3.8951
C(5)	3.8476	3.8591		
O(5)	6.2407	6.2882		
C(6)	3.8741	3.8620		
O(6)	6.2577	6.2980		

This indicates that the calculations made on (III) and (IV) to a good approximation are valid also for (I) and (II). The remaining calculations therefore are concentrated on the first two molecules.

From the structure of ascorbic acid, it is seen that O(2) might be protolyzed as well as O(3), forming the ions (V) and (VI). However, chemical evidence indicates O(3) as the protolytic group for the first protolysis.³ An attempted explanation for this is that (IV) is stabilized through resonance as shown by the structures



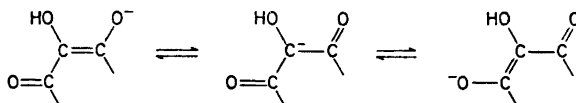
while no similar model can be made for



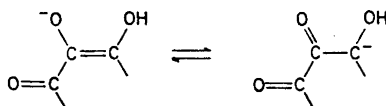
To test this resonance picture, π -electron calculations were made on (IV) and (VI). For both ions, the structure of (III) was used. From the resonance models, several predictions can be made. In (IV) the charge on O(1) will be larger than in (VI), also (VI) will have larger charge on O(2) than (IV) has on O(3). Further, in (IV) the π -bond-order for C(2)–C(3) will be smaller and for C(1)–C(2) larger than in (VI).

The result of this calculation is given in Table 7. The charge distribution is not as expected. The predicted effects are present, but they are not large enough to be considered significant. The bond orders are more as expected. The delocalized bonds implied by the resonance model for (IV) are depicted in the almost equal bond order for C(1)–C(2). In (VI) the bond is localized to C(2)–C(3).

Interesting are the high charges on C(2)/C(3) in (IV)/(VI). They indicate that if a resonance picture is used, a more complete one is



and



The π -electron energy for (VI) is 0.02 a.u. higher than for (IV). This corresponds to a Maxwell-Boltzmann distribution, at 300 K,

$$N_{\text{VI}}/N_{\text{IV}} \approx 10^{-10}$$

so the energy difference alone is satisfactory for explaining why only (II) is observed.

The lowest transition energies of (I) and (II) have been measured in aqueous solutions.¹⁸ The values found are 5.08 eV for the acid and 4.67 eV for the ion. The absorption bands have been assigned to $\pi \rightarrow \pi^*$ transitions of the ring

Table 5. The two lowest calculated transition energies, with oscillator strengths, and the lowest observed bands for (III) and (IV). Energies in eV.

	E	f	$E_{\text{obs.}}$
III	5.20	0.321	5.08
	4.84	0.212	
IV	6.34	0.156	4.67
	4.54	0.508	

electrons.¹⁸ The results of our calculations are shown in Table 5. They show that in (III) we have two transitions at 5.20 eV and 4.84 eV as the lowest values. If we take a weighted mean of these (with respect to the calculated oscillator strength f), we obtain 5.06 eV, which is close to the experimental value. For (IV) the calculation gives the lowest transition energy at 4.54 eV with oscillator strength $f=0.508$. The next transition is at 6.34 eV with $f=0.158$. It is reasonable to suppose that experimentally these two transitions will come out separately, and that the value measured corresponds to the first predicted transition.

Thus a good agreement with the experimental values is obtained. This shows that the hypothesis that the transition is $\pi \rightarrow \pi^*$ is a reasonable one, and also that the assumptions underlying the calculations used here are valid. The shift in transition energy in going from the acid to the ion is -0.41 eV. The calculated shift is -0.52 eV, in excellent agreement with the experimental value. It is somewhat surprising that the values for the ion are so well reproduced. The semi-empirical calculations are made on the isolated molecule, which means that solvent effects should be expected to give larger deviations from the theoretical values than we get here.

In the π -electron approximation, formulas have been made which give an approximate relation between mobile bond order and bond length. These are all of the form

$$R_{\mu\nu} = R_{\mu\nu}^{\circ} - cp_{\mu\nu}$$

where $R_{\mu\nu}$ is bond length, $R_{\mu\nu}^{\circ}$ is the length for a reference bond, c is a constant and $p_{\mu\nu}$ is the π -electron bond order. These relations were first used in the Hückel approximation,¹⁹ later it has been shown²⁰ that they can be used in the ZDO-SCF approximation. In this case the bonds examined are carbon-carbon,⁷ carbon-carbonyl oxygen,⁸ and carbon-hydroxyl oxygen.⁹ The formulas for these bonds are

$$R_{C-C} = 1.517 - 0.18 p_{C-C} \quad (9)$$

$$R_{C=O} = 1.365 - 0.18 p_{C=O} \quad (10)$$

$$R_{C-O} = 1.430 - 0.214 p_{C-O} \quad (11)$$

The bond orders for (III) and (IV) were used to calculate the bond lengths, and the results were compared to the experimental values for (I) and (II). The bond order is not very sensitive to changes in the input structure, so the same input as before was used. The result of these calculations are shown in Table 6.

The deviations from the experimental values are rather large. Especially for the ion, the differences are up to $0.02 - 0.03$ Å. It is interesting, however, that the changes in the bond length in the system O(1)-C(1)-C(2)-C(3) when O(3) is protolyzed, is well reproduced. The most unexpected result is that the calculated bond distances for O(2)-C(2) and O(3)-C(3) in the acid are equal. Also the difference between the calculated and the experimental value for C(3)-O(3) is 0.05 Å.

This short bond length is connected with the fact that O(3) is the protolytic oxygen. Krogh Andersen²¹ has reviewed X-ray structures of several

Table 6. Calculated bond lengths compared to experimental values. Values in Å. *a.* (III) compared to (I). *b.* (IV) compared to (II).

<i>a</i>	Bond order	Bond length	
		calc.	exp.
C(1)–C(2)	0.308	1.441	1.452
C(2)–C(3)	0.882	1.359	1.338
C(1)–O(1)	0.710	1.237	1.216
C(2)–O(2)	0.249	1.377	1.361
C(3)–O(3)	0.252	1.376	1.326
C(1)–O(4)	0.468	1.330	1.355
<i>b</i>	Bond order	Bond length	
		calc.	exp.
C(1)–O(2)	0.571	1.414	1.416
C(2)–C(3)	0.655	1.399	1.373
C(1)–O(1)	0.602	1.257	1.233
C(2)–O(2)	0.134	1.401	1.385
C(3)–O(3)	0.599	1.257	1.287
C(1)–O(4)	0.379	1.349	1.358

Table 6. *c.* Changes in bond lengths when O(3) is protolyzed. Values in Å.

	Calc.	expt.
C(1)–O(1)	+0.020	+0.017
C(1)–C(2)	–0.027	–0.038
C(2)–C(3)	+0.040	+0.035

Table 7. Charge distribution for the π -electrons and π -bond orders in (IV) and (VI).

Atom	(IV)	(IV)	Bond	(IV)	(VI)
C(1)	0.6796	0.5507	C(1)–C(2)	0.571	0.275
C(2)	1.2886	0.7998	C(2)–C(3)	0.655	0.763
C(3)	0.5749	1.3884	C(1)–O(1)	0.602	0.677
CH ₂	1.9846	1.9922	C(2)–O(2)	0.134	0.524
O(1)	1.7173	1.6768	C(3)–O(3)	0.599	0.127
O(2)	1.9748	1.7597			
O(3)	1.7248	1.9733			
O(4)	1.8760	1.8588			

organic acids, among them α -methyltetrionic acid and α,γ -dimethyltetrionic acid. A linear relation is found between the bond length of the carbon-oxygen bond and the pK_a of the oxygen.

One might argue that the short C–O distance is due to intermolecular forces, in this case hydrogen bonds. In the crystal where all the structure measurements have been made, several hydrogen bonds are present. These might cause perturbations. Against this hypothesis, however, is the fact that semi-empirical calculations made by Lofthus using the Hückel method with overlap give the correct difference in bond order.²²

REFERENCES

1. Hvoslef, J. *Acta Cryst.* **B 24** (1968) 23.
2. Hvoslef, J. *Acta Cryst.* **B 24** (1968) 1431.
3. Hvoslef, J. *Acta Cryst.* **B 25** (1969) 2214.
4. Pople, J. A., Santry D. P. and Segal, G. A. *J. Chem. Phys.* **40** (1965) S 129.
5. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* **40** (1965) S136.
6. Pople, J. A. and Segal, G. A. *J. Chem. Phys.* **44** (1966) 3289.
7. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
8. Jensen, H. and Skancke, P. N. *Acta Chem. Scand.* **22** (1968) 2899.
9. Höjer, G. *Acta Chem. Scand.* **21** (1969) 2985.
10. Roos, B. *Acta Chem. Scand.* **21** (1967) 2318.
11. Parr, R. G. *J. Chem. Phys.* **20** (1952) 1499.
12. Maggiora, G., Johansen, H. and Ingraham, L. L. *Arch. Biochem. Biophys.* **131** (1969) 352.
13. Price, W. C. and Walsh, A. D. *Proc. Roy. Soc.* **A 179** (1941) 201.
14. Schiebe, G. and Grieneisen, H. *Z. physik. Chem.* **B 25** (1934) 52.
15. Pickett, L. W., Paddock, E. and Sackter, E. *J. Am. Chem. Soc.* **61** (1941) 1073.
16. Del Bene, J. and Jaffe, H. H. *J. Chem. Phys.* **42** (1968) 4050.
17. Streitwieser, A. *J. Am. Chem. Soc.* **82** (1960) 4123.
18. Ogata, Y. and Kosugi, Y. *Tetrahedron* **26** (1970) 4711.
19. Coulson, C. A. *Proc. Roy. Soc.* **A 169** (1939) 413.
20. Skancke, P. N. *Acta Chem. Scand.* **18** (1964) 1671.
21. Krogh Andersen, E. *Experimentelle studier over hydroxyquinoner og deres salte*. Odense Universitets forlag, 1971.
22. Lofthus, A. Physical Institute, University of Oslo. *Unpublished results*.

Received April 4, 1973.