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The Structure of 6-Hydroxycrinamine

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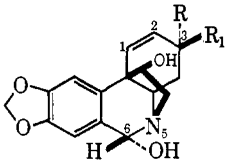
Abstract: The crystal structure analysis of 6-hydroxycrinamine by X-ray diffraction confirms the stereoconfiguration of the crinamine nucleus as derived from chemical evidence. Furthermore, it establishes that in the solid state the C-6 hydroxyl group is *trans* to the pyrrolidine ring and that the molecules occur as dimers through hydrogen bonding. Eight molecules of $C_{17}H_{19}NO_5$ crystallize in a unit cell of the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 19.33$, $b = 7.63$, and $c = 21.18$ A. The structure was solved by obtaining a partial structure with phases determined by the symbolic addition procedure and the remainder by a recycling procedure using the tangent formula.

The epimeric alkaloids 6-hydroxycrinamine (Ia) and haemanthidine (Ib), $C_{17}H_{19}NO_5$, are derived from the bulbs of the Amaryllidaceae family. The structures of their 6-deoxy derivatives have been derived from degradative and spectral evidence.[1] On the basis of further chemical and nmr studies it has been suggested that 6-hydroxycrinamine and haemanthidine each exist in solution as a mixture of C-6 epimers.[2] The X-ray diffraction analysis of a crystal of 6-hydroxycrinamine was undertaken to confirm the structure and stereoconfiguration of the crinamine nucleus and to investigate the configuration of the hydroxyl group at C-6.



Ia, R = H; $R_1 = OCH_3$
Ib, $R = OCH_3$; $R_1 = H$

Crystals of the free base were used. Since the material crystallizes with two molecules in the asymmetric unit, the structure analysis required the location of 184 atoms other than hydrogen atoms in the unit cell of a noncentrosymmetric space group. The structure determination was accomplished in a stepwise fashion. First, several atoms were located from phases determined directly from the magnitudes of the intensities by the symbolic addition procedure as applied to noncentrosymmetric crystals.[3] The remainder of the atoms was found in a recycling procedure using the tangent formula[4] and the partial structure.[5]

Experimental Section

A sample of 6-hydroxycrinamine, obtained from Fales and Wildman from the National Institutes of Health, was recrystallized from a chloroform–cyclohexane mixture. The colorless, platelike crystals were elongated in the *b* direction and could be readily cleaved in the *a* direction. Systematic absences showed the space group to be $P2_12_12_1$. Cell dimensions (A) determined from precession and powder photographs using Cu Kα radiation, $\lambda = 1.5418$ A, are $a = 19.327 \pm 0.010$, $b = 7.634 \pm 0.009$, and $c = 21.184 \pm 0.015$. The density measured with a pycnometer is 1.338 g cm^{-3} while that calculated for eight molecules per cell is 1.349 g cm^{-3}.

Intensity data were collected for seven layers on the *b* axis and four layers on the *a* axis using the multiple-film, equiinclination Weissenberg technique. Although the exposures were of the order of 50 hr, the data did not extend to the limit of the copper sphere. A total of 3521 reflections were recorded. The intensities were estimated visually by comparison with a calibrated film strip. Corrections were made for Lorentz and polarization factors and spot size. Normalized structure factor magnitudes $|E|$ as well as structure factor magnitudes $|F|$ were derived.

Structure Determination

Phase determination was begun with the relation-

$$\phi_{\vec{h}} \approx \langle \phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}} \rangle_{\vec{k}_r} \qquad (1)$$

ship[3] given in (1), where ϕ is the phase and $\vec{h}$ and $\vec{k}$ are the Miller indices, which holds for those reflections with large $|E|$ magnitudes. A measure of the reliability of eq 1 can be obtained by use of the curve of variance, Figure 2 of ref 3b. To implement eq 1, the origin of the cell was specified by assigning phases to three reflections[4] and phases of two additional reflections were specified by the symbols *a* and *b* (see Table I). A total

Table I. Phases Assigned to Implement Eq 1

$\vec{h}$	$\phi_{\vec{h}}$	$\lvert E_{\vec{h}} \rvert$
0 2 7	0	2.63
15 0 4	0	2.97
0 1 5	$+\pi/2$	2.28
9 4 12	a	3.94
7 5 8	b	3.77

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(1) H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 197 (1960).

(2) R. W. King, C. F. Murphy, and W. C. Wildman, *ibid.*, **87**, 4912 (1965).

(3) I. L. Karle and J. Karle, *Acta Cryst.*, **17**, 835 (1964); **21**, 849 (1966).

(4) J. Karle and H. Hauptman, *ibid.*, **9**, 635 (1956).

(5) J. Karle, *ibid.*, in press.

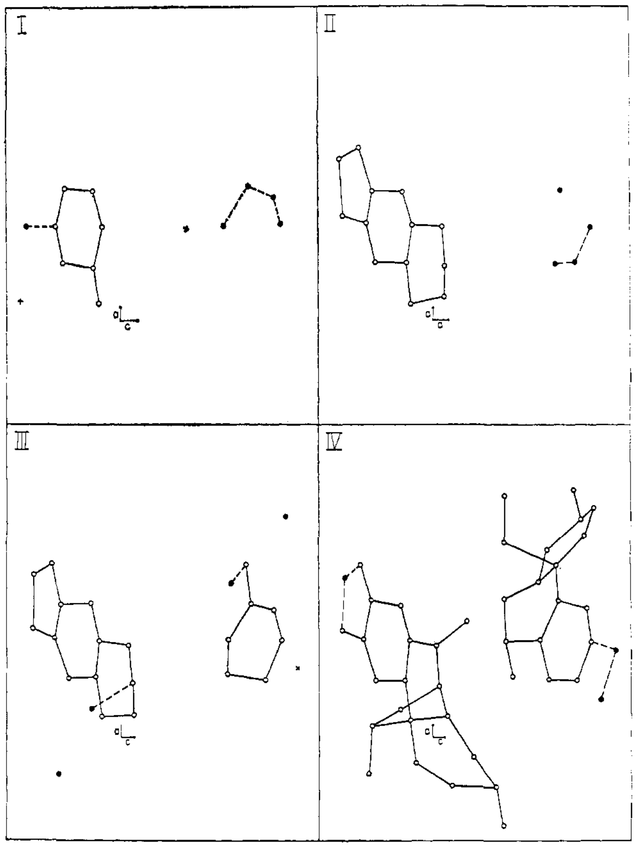

Figure 1. The open circles in part I represent the seven largest peaks in the E map computed from the phases obtained from the symbolic addition procedure. Of the seven next largest peaks, the closed circles represent meaningful peaks whereas the × marks are spurious. Only the seven atoms represented by the open circles were used to obtain initial phases for recycling the tangent formula to obtain phases for the next E map whose 17 largest peaks are shown in part II. Three repetitions of the procedure yielded the atoms shown in parts III and IV and finally all 46 atoms (not illustrated).

of 82 phases for reflections with $|E| > 1.77$ were obtained as functions of the assignments in Table I. There were several indications that the values of both a and b were real. The second trial with $a = \pi$ and $b = 0$ proved to be correct.

The 82 initial phases were refined and phases for 582 additional reflections with $|E| > 1.2$ were obtained with the tangent formula[4]

$$\tan \phi_{\vec{h}} \approx \frac{\sum_{\vec{k}} |E_{\vec{k}} E_{\vec{h}-\vec{k}}| \sin (\phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}})}{\sum_{\vec{k}} |E_{\vec{k}} E_{\vec{h}-\vec{k}}| \cos (\phi_{\vec{k}} + \phi_{\vec{h}-\vec{k}})} \qquad (2)$$

The maxima from the E map computed with these phases are shown in Figure 1, part I. The seven largest peaks are shown as open circles. Among the next largest seven peaks, five indicated as closed circles were meaningful whereas the two indicated by × were spurious. However, only the seven largest peaks, which formed a meaningful chemical unit, were used as a known partial structure to calculate structure factors. The phases for those reflections with $|E| > 1.5$ and $|F_{\text{calcd}}| > 0.20|F_{\text{obsd}}|$ were used as input data for recycling in the tangent formula, eq 2. Again phases were obtained for those reflections with $|E| > 1.2$ and a new E map computed, shown in Figure 1, part II.

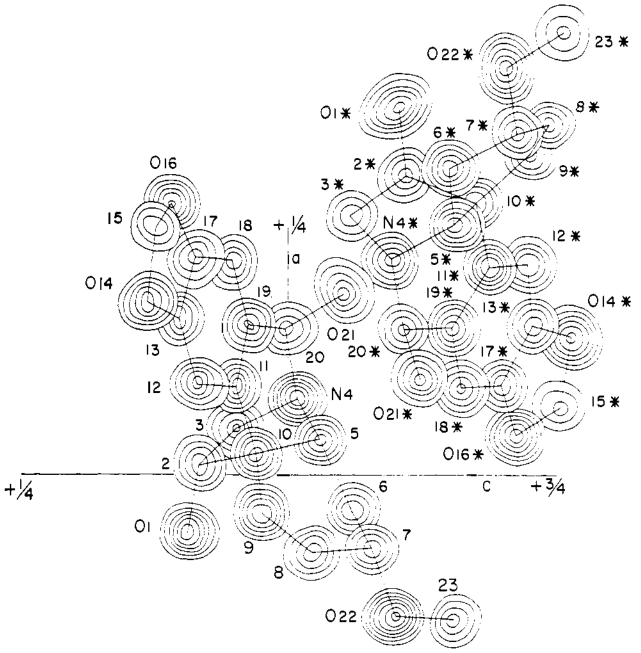

Figure 2. The electron density for an asymmetric unit of 6-hydroxycrinamine. The contours are spaced by 1.5 e/A^3 beginning with the 1.5 e/A^3 level.

Among the 17 largest peaks, 13 made the meaningful three-ring system. The other four were also correct but not used at this time as a basis for the third cycle which was performed in the same manner except that the acceptance criterion for the phases was raised to $|F_{\text{obsd}}| > 0.35|F_{\text{calcd}}|$. The progress in the third and fourth cycles is shown in Figure 1. All 46 atoms were found in the fifth cycle. The complete asymmetric unit is illustrated in Figure 2. Note that the numbering of the atoms for crystallographic identification is different from the convention used by organic chemists.

The coordinates of the 46 atoms of 6-hydroxycrinamine as found in the fifth cycle of the tangent formula were subjected to a least-squares refinement using a modified version of the ORFLS program.[6] The function minimized was $\Sigma(F_0 - F_c)^2$ and the atom form factors used were those listed in the International Tables for X-Ray Crystallography.[7] Several cycles of isotropic refinement resulted in $R = 15.9\%$. Anisotropic refinement had to be performed in two stages since the computer and the program did not have the capacity to vary all parameters simultaneously. Accordingly, in alternate cycles, one molecule of the asymmetric unit was held constant while the other was varied. After several cycles the R factor for the observed reflections was 12.6%.[8]

A difference map calculated at this stage did not show the positions of the hydrogen atoms. The final electron density map based on the phases from the last least-squares refinement is shown in Figure 2. The

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(6) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham, England, 1962.

(8) A table of the observed and calculated structure factors and the phases has been deposited as Document No. 9610 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Table II. Fractional Coordinates and Thermal Parameters for 6-Hydroxycrinamine[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule I									
O(1)	−0.0599	0.6673	0.4058	19	70	23	−13	−5	−4
C(2)	0.0107	0.7139	0.4163	16	56	17	11	−4	−11
C(3)	0.0474	0.5500	0.4490	21	41	19	5	−3	−3
N(4)	0.0785	0.6123	0.5086	14	40	17	5	−1	12
C(5)	0.0344	0.7609	0.5283	13	40	13	13	−1	7
C(6)	−0.0343	0.7005	0.5589	18	88	18	9	−1	10
C(7)	−0.0752	0.8631	0.5766	16	100	14	2	−1	10
C(8)	−0.0799	0.9892	0.5221	13	60	18	7	0	10
C(9)	−0.0371	0.9901	0.4729	11	66	16	−2	−3	2
C(10)	0.0209	0.8624	0.4672	12	38	13	−2	−2	2
C(11)	0.0912	0.9465	0.4484	12	10	16	3	0	−2
C(12)	0.0934	1.1049	0.4153	13	55	16	4	−1	9
C(13)	0.1587	1.1668	0.3991	21	49	13	−10	2	0
O(14)	0.1759	1.3189	0.3672	19	96	20	−9	3	13
C(15)	0.2496	1.3334	0.3755	17	164	22	−15	7	0
O(16)	0.2745	1.1665	0.3900	18	134	20	−9	5	6
C(17)	0.2191	1.0731	0.4133	17	127	16	−1	3	−11
C(18)	0.2164	0.9156	0.4444	17	85	20	5	0	2
C(19)	0.1523	0.8564	0.4618	12	53	15	8	1	−6
C(20)	0.1483	0.6821	0.4990	17	32	24	10	−1	15
O(21)	0.1848	0.7079	0.5526	32	184	28	5	−8	12
O(22)	−0.1448	0.8233	0.5959	15	137	16	−9	0	11
C(23)	−0.1485	0.7353	0.6556	28	163	14	−10	4	15
Molecule II									
O(1)*	0.3764	0.1668	0.6006	22	101	36	−5	18	−3
C(2)*	0.3040	0.1307	0.6078	20	88	21	1	8	−2
C(3)*	0.2617	0.2431	0.5604	31	203	15	−2	2	−5
N(4)*	0.2171	0.3650	0.5950	17	127	14	−4	−6	22
C(5)*	0.2511	0.3884	0.6574	12	87	13	6	−2	12
C(6)*	0.3109	0.5165	0.6512	13	79	15	−4	1	−4
C(7)*	0.3494	0.5252	0.7153	20	143	16	−19	−2	3
C(8)*	0.3594	0.3500	0.7441	17	230	17	−20	−7	19
C(9)*	0.3274	0.2056	0.7269	16	134	21	3	−7	19
C(10)*	0.2747	0.2035	0.6731	9	81	14	6	−2	14
C(11)*	0.2107	0.0930	0.6859	11	68	11	4	0	12
C(12)*	0.2113	−0.0552	0.7244	14	105	18	−1	−3	14
C(13)*	0.1512	−0.1519	0.7292	21	69	16	−10	−1	14
O(14)*	0.1402	−0.3032	0.7626	28	151	29	−30	−10	47
C(15)*	0.0688	−0.3460	0.7528	28	219	41	−34	−9	60
O(16)*	0.0391	−0.2209	0.7122	19	123	26	−17	−4	21
C(17)*	0.0916	−0.1020	0.6990	16	108	17	−10	0	6
C(18)*	0.0879	0.0446	0.6617	18	92	14	−1	−3	4
C(19)*	0.1497	0.1379	0.6537	13	69	13	3	0	11
C(20)*	0.1483	0.2822	0.6043	15	136	26	−5	−4	39
O(21)*	0.0999	0.4034	0.6203	23	226	39	13	−1	50
O(22)*	0.4150	0.6104	0.7013	23	188	16	−30	0	−1
C(23)*	0.4482	0.6863	0.7572	41	368	25	−80	−3	−16
Standard Deviations									
C	0.0006	0.0017	0.0005	3	24	3	7	2	6
N	0.0004	0.0013	0.0004	2	19	2	6	2	5
O	0.0004	0.0013	0.0004	2	21	3	6	2	6

[a] The thermal parameters are of the form $T = \exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl])$. Each thermal parameter is multiplied by 10^4. [b] The coordinates in Table II may be substituted directly into the equations given in footnote *c* of Table V to obtain the deviations.

fractional coordinates and thermal parameters for the carbon, nitrogen, and oxygen atoms are listed in Table II.

Discussion

The configuration of the molecules and the packing in the unit cell are illustrated in the stereodiagrams in Figures 3 and 4. The X-ray results confirm the configuration for the crinamine nucleus as obtained from degradative studies.[1] Even though there are two independent molecules in the asymmetric unit of the crystal, the geometry of the two molecules is quite similar. The C-6 hydroxyl groups (labeled in this paper as atoms O(21) and O(21)*) are *trans* to the pyrrolidine rings in both molecules. Therefore in contrast to the proposal based on nmr studies that 6-hydroxycrinamine exists as a mixture of C-6 epimers in solution,[2] there is no evidence of epimers in the solid state. Rather, in the crystal, the two molecules are associated into dimers by a pair of hydrogen bonds between N(4)-O(21)* and N(4)*-O(21), 2.84 and 2.88 A, respectively, as shown in Figure 3. The hydrogen bonds to the nitrogen atoms, N(4) and N(4)*, provide the fourth bond linkage in a tetrahedral configuration. There is the possibility that the molecule exists as a zwitterion with the proton on the nitrogen atom rather than on the hydroxyl. Regrettably, the crystals and the scattering data were not sufficiently good to permit

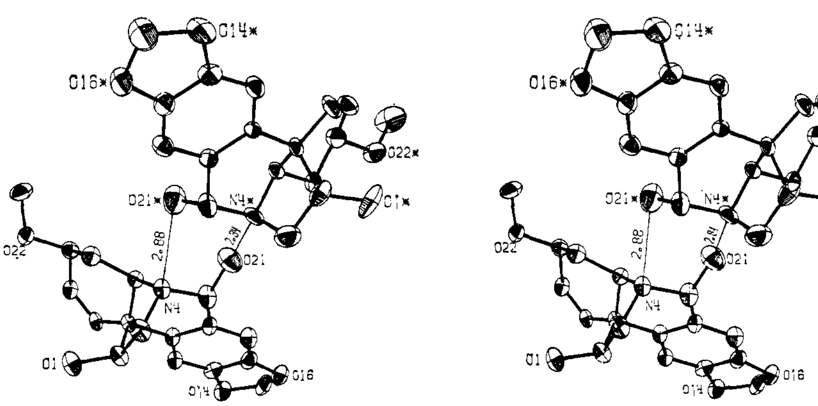

Figure 3. Stereoscopic diagrams of the dimeric unit of 6-hydroxycrinamine. The drawing was made by a computer program prepared by C. K. Johnson, ORTEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965. These diagrams are to be viewed with a simple hand viewer obtainable, *e.g.*, from Stereo-Magniscope, Inc., Elmhurst, N. Y.

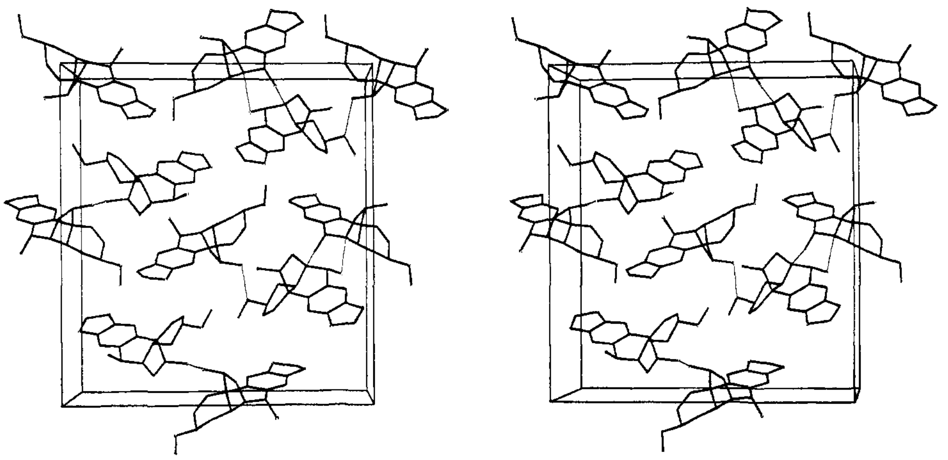

Figure 4. Stereoscopic diagrams of the contents of the unit cell. The origin is in the middle with the *a* axis →, the *c* axis ↓, and the *b* axis up from the page.

the location of the hydrogen atoms. However, the short aliphatic C(20)–O(21) and C(20)*–O(21)* bond lengths of ~1.35 A (Figure 5), as compared to normal

Table III. Bonded Interatomic Distances (A)

	Molecule I	Molecule II
O(1)–2	1.428	1.435
2–3	1.595	1.553
3–N(4)	1.477	1.463
N(4)–5	1.479	1.486
5–10	1.530	1.520
10–2	1.577	1.593
5–6	1.549	1.520
6–7	1.518	1.549
7–8	1.505	1.482
8–9	1.329	1.315
9–10	1.491	1.529
10–11	1.555	1.521
11–19	1.396	1.405
19–20	1.548	1.519
20–N(4)	1.464	1.486
11–12	1.398	1.394
12–13	1.390	1.380
13–17	1.401	1.373
17–18	1.372	1.371
18–19	1.370	1.401
13–O(14)	1.384	1.371
O(14)–15	1.439	1.433
15–O(16)	1.395	1.407
O(16)–17	1.379	1.390
20–O(21)	1.349	1.359
7–O(22)	1.438	1.455
O(22)–23	1.432	1.465

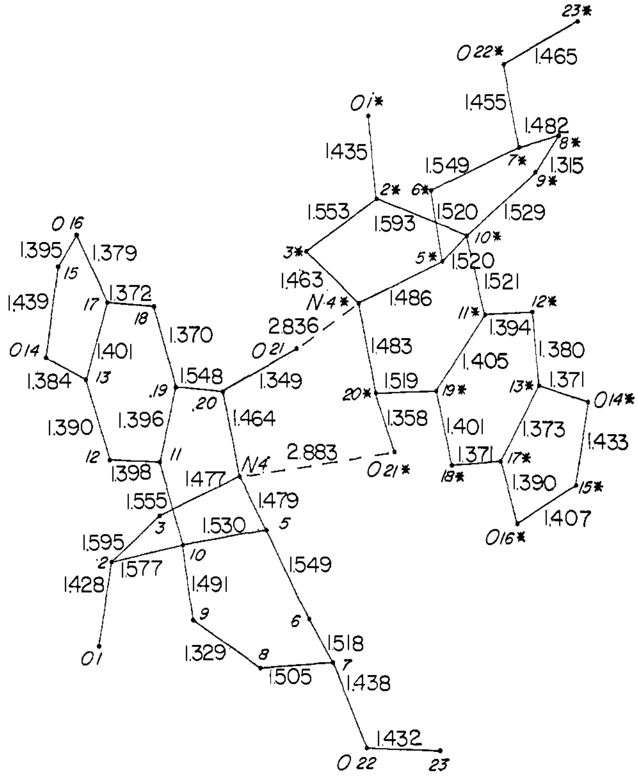

Figure 5. Bond lengths in 6-hydroxycrinamine.

Table IV. Bond Angles (degrees)

	Molecule I	Molecule II
O(1)-2-3	107.3	109.9
O(1)-2-10	113.9	111.8
3-2-10	102.2	100.5
2-3-N(4)	107.5	109.7
3-N(4)-5	104.6	105.2
3-N(4)-20	112.0	108.8
5-N(4)-20	106.9	109.2
N(4)-5-6	112.6	109.7
N(4)-5-10	104.3	102.5
6-5-10	111.0	112.7
5-6-7	107.9	108.5
6-7-8	111.4	112.6
6-7-O(22)	112.6	105.1
8-7-O(22)	107.3	111.9
7-8-9	124.6	125.5
8-9-10	121.8	121.9
2-10-5	103.6	103.9
2-10-9	115.5	114.5
2-10-11	103.3	104.5
5-10-9	113.0	110.7
5-10-11	106.1	108.0
9-10-11	114.1	114.5
10-11-12	120.8	123.2
10-11-19	119.0	117.5
12-11-19	120.1	119.2
11-12-13	116.5	118.1
12-13-O(14)	128.6	128.4
12-13-17	122.0	121.6
O(14)-13-17	109.4	110.1
13-O(14)-15	104.0	105.5
O(14)-15-O(16)	107.4	109.1
15-O(16)-17	106.4	105.5
O(16)-17-18	130.8	127.6
13-17-18	121.3	122.6
O(16)-17-13	107.9	109.8
17-18-19	116.8	116.1
18-19-20	117.7	115.6
18-19-11	123.3	122.2
11-19-20	119.0	121.8
19-20-O(21)	106.1	109.5
19-20-N(4)	115.4	112.5
N(4)-20-O(21)	114.7	111.1
7-O(22)-23	113.5	113.3

Table V. Least-Squares Planes[a,c] and Deviations

Plane A		Plane B		Plane C		Plane D	
Atom	Δ, A	Atom	Δ, A	Atom	Δ, A	Atom	Δ, A
N(4)	−0.137[b]	N(4)*	−0.386[b]	2	+0.024	2*	+0.010
10	−0.055[b]	10*	−0.073[b]	3	−0.026	3*	−0.010
11	+0.007	11*	+0.003	N(4)	+0.018	N(4)*	+0.007
12	−0.015	12*	+0.021	5	−0.601[b]	5*	+0.624[b]
13	+0.006	13*	+0.001	10	−0.016	10*	−0.007
O(14)	+0.004	O(14)*	−0.020				
15	+0.313[b]	15*	0.000				
O(16)	−0.003	O(16)*	−0.002				
17	+0.005	17*	+0.010				
18	−0.008	18*	+0.021				
19	+0.005	19*	−0.035				
20	+0.096[b]	20*	+0.248[b]				

[a] See Table II, footnote *b*. [b] These atoms were not included in obtaining the equations for the least-squares planes. [c] A, $1.3849x + 3.7028y + 18.4629z = 11.9031$; B, $-5.1077x + 4.2115y + 16.7582z = 10.8067$; C, $16.3355x + 1.9925y - 9.8792z = -2.5398$; D, $14.0849x + 5.2267y + 0.2497z = 5.1071$.

aliphatic C–OH values of $\sim$1.43 A, as in C(2)–O(1) and C(2)*–O(1)*, may lend support to the proposal that a zwitterion is formed.

Bond lengths and angles are shown in Tables III and IV and in Figure 5. The standard deviations are 0.017 A for the bond lengths and 1° for the angles as derived from the least-squares refinement alone. To account for all the other possible experimental errors, these values should probably be doubled. The comparable parameters in the two molecules are quite similar with no significant differences. The values of the bond lengths and angles are normal.

The five-membered rings containing N(4) and N(4)* have the configuration usually found for saturated five-membered rings in that four atoms are in a plane and the fifth one is $\sim$0.6 A out of the plane. Columns for planes C and D in Table V show the deviations of the atoms from least-squares planes computed for these rings. It would be expected that the benzene rings be planar and that the adjacent five-membered rings be coplanar with them. This is true for molecule II where atoms 11*–19* are within $\pm$0.03 A of the least-squares plane adjusted to them, plane B in Table V. However, for molecule I, C(15) is +0.31 A out of the plane while the remainder of the atoms 11–19 are within $\pm$0.015 A of plane A. A possible reason for this distortion is the proximity of C(15) to O(14)* of a neighboring molecule. With the bending of C(15) out of the plane, the C(15)...O(14)* distance is 3.21 A. Without the distortion the intermolecular approach would be 3.0 A.

There are two other close approaches between molecules each involving only oxygen atoms. The O(1)···O(1)* distance, illustrated by a light line near the bottom of Figure 4, is 2.83 A. Since this close approach is between hydroxyl groups, it can be assumed that a hydrogen bond is formed. The O(1)···O(22)* distance, illustrated by the light line in the upper right-hand corner of Figure 4, is also only 2.87 A. However, O(22)* is part of a methoxy group and hydrogen bonding is not expected. A similarly close approach between a $-OCH_3$ group and a H_2O molecule has been found in the crystal of codeine–HBr–$2H_2O$.[9] These close approaches must be van der Waal contacts.

The ellipsoids in Figure 3 represent the relative thermal motion of the atoms. In general, the atoms in the central portions of the molecules are held much more rigidly than those on the periphery. The hydroxyl groups and the carbons of the methoxy groups have rather large and anisotropic motions.

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(9) J. M. Lindsey and W. H. Barnes, *Acta Cryst.* **8**, 227 (1955).

to Dr. H. Norment who collected the diffraction data and prepared it for phase determination and to Mr. S. Brenner who prepared the reiteration program using the tangent formula.

Chemiluminescence from Reactions of Electronegatively Substituted Aryl Oxalates with Hydrogen Peroxide and Fluorescent Compounds[1]

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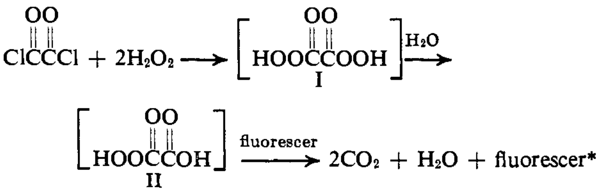
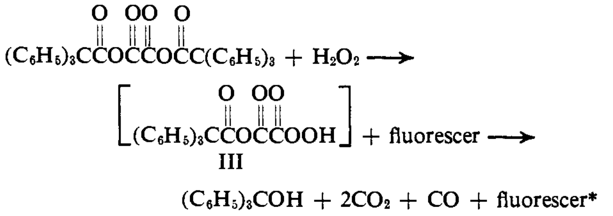
Abstract: Reactions of a series of oxalate esters with hydrogen peroxide and fluorescent compounds were examined for chemiluminescent light emission. Electronegatively substituted aryl oxalate esters were found capable of generating light with high efficiency; a quantum yield of 0.23 einstein mole^{-1} was obtained from bis(2,4-dinitrophenyl) oxalate, hydrogen peroxide, and rubrene. Comparison of chemiluminescence with fluorescence spectra indicates that the first singlet excited state of the fluorescer is the emitting species. The effects of ester, peroxide, and fluorescer structures and concentrations are reported. The reaction stoichiometry was found to be 1:1 ester:H_2O_2. The chemiluminescence efficiency is strongly dependent on the fluorescer structure. It was shown that a long-lived chemiluminescent intermediate is produced in the absence of fluorescer, and that the fluorescer catalyzes its decomposition. A tentative mechanism is discussed in terms of this and other evidence.

Chemiluminescence has been reported from reactions of hydrogen peroxide with oxalyl chloride[2,3] and certain mixed oxalic anhydrides[4] in the presence of fluorescent organic compounds such as 9,10-diphenylanthracene (DPA) (eq 1 and 2).



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl} + 2H_2O_2 \longrightarrow \left[\underset{\mathrm{I}}{\mathrm{HOO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}}\right] \xrightarrow{H_2O} \left[\underset{\mathrm{II}}{\mathrm{HOO\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OH}}\right] \xrightarrow{\text{fluorescer}} 2CO_2 + H_2O + \text{fluorescer}^* \quad (1)$$



$$\mathrm{(C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}C(C_6H_5)_3} + H_2O_2 \longrightarrow \left[\underset{\mathrm{III}}{\mathrm{(C_6H_5)_3C\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OOH}}\right] + \text{fluorescer} \longrightarrow (C_6H_5)_3COH + 2CO_2 + CO + \text{fluorescer}^* \quad (2)$$

Under suitable conditions these chemiluminescent reactions are substantially more efficient than those previously reported; light yields near 5 and 13%, respectively, have been obtained from reactions 1[3] and 2[4] in contrast to yields of 1% or less obtained from earlier reactions.[5] In reactions 1 and 2 the spectrum of the emitted light matches the normal fluorescence spectrum of the added fluorescer, indicating that the first singlet excited state of the fluorescer is the emitting species.[3,4] The results of a mechanism study of reaction 1 suggested that diperoxyoxalic acid (I) and monoperoxyoxalic acid (II) were intermediates in the chemiluminescent process, at least when carried out in ether solution.[3] A preliminary study of anhydride reaction 2 did not rule out intermediates I and II, but suggested that monoanhydride III was a possible intermediate.[4] Both mechanisms were consistent with the suggestion that concerted multiple bond cleavage decomposition of a key intermediate was essential to accommodate the substantial and simultaneous energy release required for fluorescer excitation.[6]

Providing that the essential elements of mechanisms 1 and 2 are valid, it would appear that oxalic peracids meeting the concerted decomposition requirement are particularly efficient sources of electronic excitation energy in chemiluminescence. If so, then other reactions generating such peroxyoxalates in the presence of a fluorescer should be capable of efficient chemiluminescence, providing competing, nonluminescent side reactions are minimized. To examine this point we have investigated the reactions of a series of oxalate esters with hydrogen peroxide in the presence of organic fluorescers.

Results

Preliminary Survey of Oxalate Esters for Chemiluminescence. The scope of oxalate ester chemiluminescence was quickly surveyed by visually observing the reactions of 20 esters (about 0.005 *M*) with anhydrous

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[1] Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Abstract O-169.

[2] E. A. Chandross, *Tetrahedron Letters*, 761 (1963).

[3] M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).

[4] L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, *ibid.*, **89**, 6523 (1967).

[5] For reviews see: F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966); K. D. Gunderman, *Angew. Chem., Intern. Ed. Engl.*, **4**, 566 (1965); V. I. Papisova, V. Y. Shlyapintokh, and R. F. Vasl'ev, *Russ. Chem. Rev.*, **34**, 599 (1965); E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964).

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