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Structures and Interconversion of Polymorphs of 2,3-Dichloroquinizarin. Use of Second Harmonic Generation To Follow the Change of a Centrosymmetric to a Polar Structure

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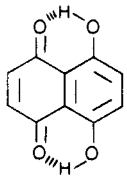
Abstract: 2,3-Dichloroquinizarin has been found to exist in two crystalline forms. One, centrosymmetric, rearranges to the other (polar) on heating. The transformation can be followed by SHG as well as the more conventional methods of infrared spectroscopy and DSC. Crystal structures of both polymorphs have been determined. The first is in space group $P2_1/c$ with $a = 12.309$ (4) Å, $b = 5.089$ (2) Å, $c = 22.690$ (5) Å, $\beta = 122.53$ (3)°, $Z = 4$. The structure was solved by direct methods and refined to $R = 0.044$ for the 1021 non-zero reflections recorded. The structure of the second, in space group Pc with $a = 3.788$ (2) Å, $b = 9.070$ (5) Å, $c = 17.252$ (9) Å, $\beta = 93.69$ (4)°, $Z = 2$, was solved by direct methods and refined to $R = 0.037$ for the 1031 non-zero reflections recorded. The crystal packings of these two, as well as the structural change required by the conversion of the centrosymmetric to the noncentric form, have, remarkably, features in common with the centrosymmetric and (low temperature) polar forms of naphthazarin C. The structure of the centrosymmetric dichloroquinizarin is also quite similar to that of the unsubstituted form already in the literature.

Thermally induced transformations of molecular crystals in the solid state have been extensively investigated[1] and may involve changes at the molecular level ranging from nil (as in many phase transitions)[2] on the one hand to drastic molecular rearrangement on the other.[3] Of particular interest are those transformations in which a fundamental change of symmetry occurs, particularly a change from a centrosymmetric to a chiral or polar structure.[4] Thus, not only have dihydroxynaphthoquinone (naphthazarin, **1**) and its derivatives shown a remarkable tendency to exist in a variety of crystalline forms but naphthazarin C on cooling to 110 K has been shown to undergo a single-crystal to single-crystal transition from a centrosymmetric structure (space group $P2_1/c$) to a polar structure (Pc).[5]



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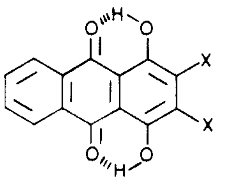

2: X=H
3: X=Cl

Most noncentrosymmetric crystals have the important property of doubling the frequency of a beam of laser light (second harmonic generation (SHG)).[6] The utility of SHG in the study of a phase transition from a noncentrosymmetric crystalline substance to a centrosymmetric polymorph was indicated by the work of Dougherty and Kurtz,[7] who in 1976 reported its use to follow the disappearance of the second harmonic signal as phenanthrene underwent a transition from its room temperature structure (space group $P2_1$) to a high-temperature-stable phase. The reaction was readily reversed with reappearance of the second harmonic when the temperature was lowered. The structure of the high-temperature form is apparently still unknown but may be presumed from the SHG results to be centrosymmetric. SHG has also been employed to study the phase transition of ferroelectric lithium tantalate by Bergman,[8] who suggested that the technique might be generally useful for following phase transitions. Nevertheless there seems to have been little if any application since that time of SHG to the study of rearrangements of molecular crystals.

In the course of our study of naphthazarin and its derivatives we were attracted to the related substance, 1,4-dihydroxyanthraquinone (**2**), commonly known as quinizarin, since it had been found to exist in a centrosymmetric form (**2A**), space group $P2_1/c$, stable at room temperature, whose structure was known[9] and also in a polar form (**2B**), space group Pc,[10] of unknown structure, obtained by crystallization from the melt. Crystals of **2B** were reported to revert to **2A** on standing at room temperature, but the interconversion was not studied further.

We have found that the 1,2-dichloro derivative **3** not only shows dimorphism similar to that of the unsubstituted compound **2** but crystals of each of the two forms **3A** and **3B** suitable for structure determination can be readily obtained and are stable at room temperature. This paper reports the crystal structures of **3A** and **3B** as well as a preliminary study of the conversion on heating of the centrosymmetric to the polar form and the use of SHG to follow this conversion.

Quinizarin and some related compounds have been shown in early work of Pfeiffer and his collaborators[11] to undergo reaction in the crystalline state with ammonia vapor to form unstable complexes. Because of our earlier interest[12] in the anisotropy of related solid–gas reactions we have investigated the reaction of single crystals of **3A** with ammonia vapor and the correlation with

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[1] (a) Curtin, D. Y.; Paul, I. C.; Duesler, E. N.; Lewis, T. W.; Mann, B. J.; Shiau, W.-I. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 25–41. (b) Byrn, S. R. *Solid-State Chemistry of Drugs*; Academic: New York, 1982. (c) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. *Advances in Physical Organic Chemistry*; Academic: New York, 1977; Vol. 15, pp 63 ff.

[2] McCrone, W. C. *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Interscience: New York, 1965, Vol. II, Chapter 8.

[3] (a) Pendergrass, D. B., Jr.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 8722–8730. (b) *Ibid.* **1972**, *94*, 8730–8737.

[4] (a) Paul, I. C.; Curtin, D. Y. *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; Chapter 9. (b) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525–541.

[5] (a) Herbstein, F. H.; Kapon, M.; Reisner, G. M.; Lehman, M. S.; Kress, R. B.; Wilson, R. B.; Shiau, W. I.; Duesler, E. N.; Paul, I. C.; Curtin, D. Y. *Proc. R. Soc. London* **1985**, *A399*, 295–319. (b) Pascard-Billy, C. *Bull. Soc. Chim. Fr.* **1962**, 2293–2298. (c) *Ibid.* **1962**, 2282–2293. (d) *Ibid.* **1962**, 2299–2312. (e) Cradwick, P. D.; Hall, D. *Acta Crystallogr.* **1971**, *B27*, 1990–1997.

[6] (a) *Non-linear Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; American Chemical Society; Washington, DC, 1983. (b) *Non-linear Optical Properties of Organic Molecules and Crystals*; Chemal, D. S., Zyss, J., Eds.; Academic: Orlando, 1987; 2 volumes.

[7] Dougherty, J. P.; Kurtz, S. R. *J. Appl. Crystallogr.* **1976**, *9*, 145–158.

[8] Bergman, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 1054–1055.

[9] See: Nigam, G. D.; Deppisch, G. D. *Z. Krist.* **1980**, *151*, 185–191.

[10] Borgen, O. *Acta Chem. Scand.* **1966**, *20*, 2885–2886.

[11] Pfeiffer, P.; Angen, O.; Wang, L.; Seydal, R.; Quehl, K. *J. Prakt. Chem.* [*2*] **1930**, *126*, 97–145.

[12] See ref 1b and Paul and Curtin (Paul, I. C.; Curtin, D. Y. *Science* **1975**, *187*, 19–26) for a discussion of earlier work in this area.

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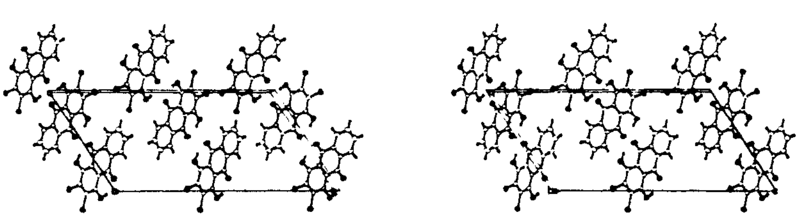

Figure 1. Stereo-pair drawing of the crystal structure of 2,3-dichloroquinizarin (**3A**). The *b* axis is oriented with +*b* out from the plane of the page; *c* is to the left and *a* down and to the right in the plane of the page.

the internal structure of the crystal.

Experimental Section

Microanalyses were carried out by J. Nemeth and his associates. Fourier transform infrared spectra were obtained in Nujol mull with a Nicolet 7000 FTIR spectrophotometer or IBM IR/32 FTIR spectrophotometer. Differential scanning calorimetry scans were recorded with a DuPont 900 thermal analyzer. DSC temperatures reported are extrapolated onset values. X-ray powder photographs (Ni-filtered Cu Kα radiation) were made with a Debye–Scherrer powder camera. Optical goniometric data were measured on a Tecom two-circle optical goniometer. Photographs were taken with a Beseler Topcon Super D camera mounted on a Bausch and Lomb Model LS dynoptic polarizing microscope with 160 ASA Ektachrome film.

2,3-Dichloroquinizarin (3)[13a] was prepared by addition of equimolar amounts (0.01 mol) of 1,4-dihydroxynaphthalene and dichloromaleic anhydride to a molten mixture at 130 °C of aluminum chloride (21 g) diluted with 10% of its weight of sodium chloride in a modification of the procedure employed previously[13b] for the unsubstituted quinizarin. After 1 min at 130 °C the mixture was cooled, poured into ice water, made acidic with 10% concentrated HCl, and allowed to stand for 12 h. The orange-brown solid was collected by filtration and sublimed to give, in a yield of 56%, the desired quinizarin: mp 248 °C (lit.[13c] mp 249–251 °C); FTIR (**3A**) (Nujol) (peaks most useful for distinguishing the two forms in boldface type) 1629 (sh 1638), 1588, 1409, 1351, 1331, **1251** (sh 1268), 1107, 1039, 1018, 920, 857, **797** cm^{-1}; (**3B**) (Nujol) 1628 (sh 1640), 1587, 1418, 1341, **1292**, 1260, **1230**, 1107, 927, 816, 787, 668, 657 cm^{-1}; mass spectrum, *m/e* 307.8 (M^+ 100), 272.9 (22.3), 157.0 (9.98), 126.0 (12.45).

When **3** was recrystallized from chloroform at room temperature, orange six-sided prisms of **3A** were obtained. Recrystallization of **3** by rapidly cooling a warm (50–80 °C) toluene solution or crystallization from warm chloroform produced darker orange needles or plates of **3B**.

X-ray Structure Determination of 2,3-Dichloroquinizarin (Form A). Crystals of **3A** suitable for X-ray work were obtained by crystallization from chloroform. The space group and preliminary unit cell dimensions were obtained from precession photographs.

Crystal data: $C_{14}H_6Cl_2O_4$, mol wt = 308.9; monoclinic; a = 12.309 (4) Å, b = 5.089 (2) Å, c = 22.690 (5) Å, β = 122.53 (3)°; V = 1198.6 (8) × 10^{-24} cm^3; Z = 4; D_{calcd} = 1.72 g/cm^3; $F(000)$ = 624; systematic absences, $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$; space group $P2_1/c$. Final unit cell parameters were determined by a least-squares fit to the settings of 15 accurately centered high-order reflections (Mo Kα = 0.71069 Å).

Intensity data were collected on a Syntex P2$_1$ four-circle diffractometer with a graphite monochromator and Mo Kα radiation. Of the 3187 unique reflections so obtained, 1021 had intensities greater than $2.58\sigma(I)$ in the 2θ range of 3–55°. An extinction correction (0.004) and an analytical absorption correction (transmission coefficient range 0.91–0.87, maximum to minimum) were made. No evidence of crystal decomposition was detected.

The weighting scheme used was $2.424/(\sigma^2(F_o) + (0.0006(F_o)^2))$, where σ is the standard deviation from counting statistics. Atomic scattering factors were those in the *International Tables for X-ray Crystallography*.[14]

The structure was solved with the MULTAN[15] series of programs. Least-squares refinement involving positional and anisotropic thermal parameters for the non-hydrogen atoms gave an R factor of 0.061.[16] The positions of the hydrogen atoms were determined from a difference map.

Table I. Atomic Coordinates for **3A**

	x/a	y/b	z/c
Cl2	0.0196 (1)	0.6033 (3)	0.30260 (6)
Cl3	−0.1797 (1)	0.2264 (3)	0.30505 (7)
O1	0.2799 (4)	0.5160 (7)	0.4122 (2)
O4	−0.0686 (3)	−0.1493 (7)	0.4160 (2)
O9	0.4606 (3)	0.2772 (7)	0.5205 (2)
O10	0.1208 (3)	−0.3746 (6)	0.5245 (2)
C1	0.2025 (5)	0.3442 (9)	0.4170 (2)
C2	0.0685 (5)	0.3654 (9)	0.3659 (2)
C3	−0.0181 (4)	0.2000 (9)	0.3677 (2)
C4	0.0226 (5)	0.0064 (9)	0.4191 (2)
C5	0.3797 (5)	−0.412 (1)	0.6335 (3)
C6	0.5084 (6)	−0.423 (1)	0.6861 (3)
C7	0.5946 (6)	−0.253 (1)	0.6850 (3)
C8	0.5541 (5)	−0.075 (1)	0.6320 (3)
C9	0.3813 (5)	0.133 (1)	0.5220 (3)
C10	0.1976 (4)	−0.218 (1)	0.5242 (2)
C1a	0.2435 (5)	0.1538 (9)	0.4683 (2)
C4a	0.1541 (5)	−0.0176 (9)	0.4702 (2)
C5a	0.3370 (4)	−0.2303 (10)	0.5798 (2)
C8a	0.4242 (5)	−0.0607 (9)	0.5786 (2)
H1	0.370 (7)	0.46 (1)	0.450 (4)
H4	−0.032 (5)	−0.26 (1)	0.451 (3)
H5	0.323 (4)	−0.524 (9)	0.634 (2)
H6	0.535 (5)	−0.55 (1)	0.720 (3)
H7	0.679 (6)	−0.25 (1)	0.719 (3)
H8	0.607 (5)	0.05 (1)	0.629 (2)

A full-matrix least-squares refinement varying positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms reached convergence with R = 0.044, R_w = 0.035, and GOF = 1.36.[17] The final electron density difference map revealed no significant electron density greater than 0.45 e$^-$/Å^3. The crystal structure is shown in Figure 1 and atomic coordinates are given in Table I. A list of observed and calculated structure factors and a table of anisotropic thermal parameters have been deposited as supplementary material.

X-ray Structure Determination of 2,3-Dichloroquinizarin (Form B). Crystals of **3B** suitable for X-ray work were obtained by crystallization from warm chloroform. Crystal symmetry and preliminary unit cell dimensions were obtained from precession photographs.

Crystal data: $C_{14}H_6Cl_2O_4$, mol wt = 308.9; monoclinic; a = 3.788 (2) Å, b = 9.070 (5) Å, c = 17.252 (9) Å, β = 93.69 (4)°; V = 591.9 (6) × 10^{-24} cm^3; Z = 2; D_{calcd} = 1.74 g/cm^3; $F(000)$ = 312; systematic absences, $h0l$ when $l = 2n + 1$; space group Pc (or $P2/c$). $P2/c$ was rejected because the molecular C_2 axis is too long for the unique axis of the unit cell. The noncentrosymmetry required by space group Pc was verified by SHG and pyroelectric tests. Final unit cell dimensions were determined by a least-squares fit to the settings of 15 accurately centered high-order reflections ((Mo Kα = 0.71069 Å).

Intensity data were collected on a Syntex P2$_1$ four-circle diffractometer with a graphite monochromator and Mo Kα radiation. Of the 1479 reflections so obtained, 1031 had intensities greater than 2.58σ(I) in the 2θ range of 3–55°. No extinction or absorption correction was made. No evidence of crystal decomposition was detected.

The weighting scheme used was $1.826/(\sigma^2(F_o) + (0.0007(F_o)^2))$, where σ is the standard deviation from counting statistics. Atomic scattering factors were those in the *International Tables for X-ray Crystallography*.[14]

The structure was solved with the MULTAN[15] series of programs. Least-squares refinement involving positional and anisotropic thermal parameters for the non-hydrogen atoms gave an R factor of 0.041.[16] The

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[13] (a) Hoechster, Farbwerken, German Patent 172 105 (1896) [*Beilstein's Handbook*, **1925**, *8*, 452]. (b) Zahn, K.; Ochwat, P. *Liebigs Ann. Chem.* **1928**, *462*, 72–97. (c) Swaminathan, S.; Nigam, G. D. *Curr. Sci.* **1967**, *36* (20), 541–545.

[14] Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

[15] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *A27*, 368–376.

[16] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

[17] "Goodness of Fit" = $(\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$.

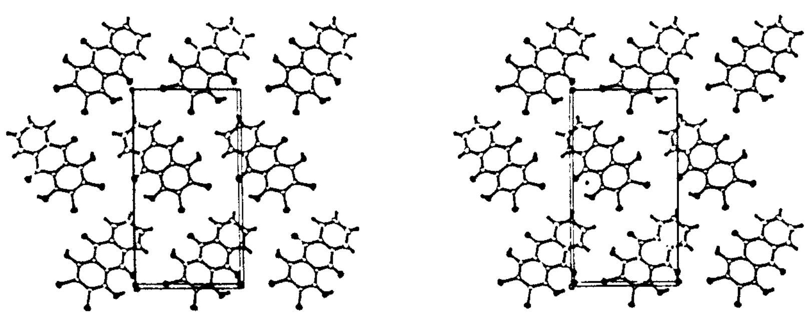


Figure 2. Stereo-pair drawing of the crystal structure of 2,3-dichloroquinizarin (3B). The *a* axis is oriented with +*a* out of the page; *c** is up and *b* to the right in the page.

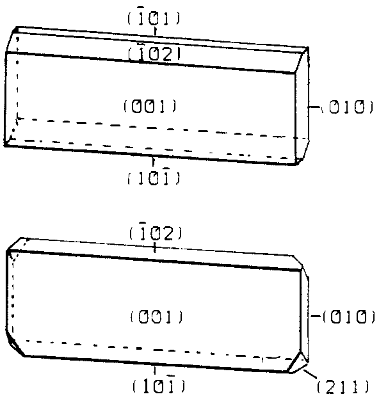


Figure 3. Crystal morphology of **3A**. The upper drawing shows the principal faces. The lower drawing shows the oblique face, possibly belonging to {211} found in the crystal undergoing reaction (Figure 4). The *a* and *b* axes lie in the plane of the page with *a* down and *b* to the right.

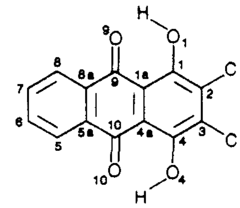
Table II. Atomic Coordinates for **3B**

	x/*a*	*y*/*b*	*z*/*c*
Cl2	1.2195	0.4474 (2)	0.3851
Cl3	1.2094 (5)	0.7099 (1)	0.5049 (1)
O1	0.939 (1)	0.1777 (5)	0.4404 (2)
O4	0.937 (1)	0.6312 (4)	0.6498 (2)
O9	0.653 (1)	0.0143 (4)	0.5385 (3)
O10	0.651 (1)	0.4593 (4)	0.7443 (2)
C1	0.933 (1)	0.2822 (5)	0.4938 (3)
C2	1.059 (1)	0.4234 (5)	0.4754 (3)
C3	1.056 (1)	0.5376 (5)	0.5272 (3)
C4	0.931 (1)	0.5165 (5)	0.6020 (3)
C5	0.466 (2)	0.1794 (7)	0.7962 (3)
C6	0.366 (2)	0.0406 (7)	0.8168 (4)
C7	0.360 (2)	−0.0737 (7)	0.7640 (4)
C8	0.456 (2)	−0.0507 (6)	0.6897 (4)
C9	0.673 (1)	0.1142 (6)	0.5871 (3)
C10	0.674 (1)	0.3552 (6)	0.6987 (3)
C1a	0.806 (1)	0.2596 (5)	0.5677 (3)
C4a	0.807 (1)	0.3774 (5)	0.6219 (3)
C5a	0.567 (1)	0.2053 (5)	0.7202 (3)
C8a	0.561 (1)	0.0892 (5)	0.6668 (3)
H1	0.87 (2)	0.103 (8)	0.455 (4)
H4	0.82 (2)	0.60 (1)	0.687 (6)
H5	0.51 (1)	0.251 (6)	0.833 (3)
H6	0.33 (2)	0.021 (8)	0.857 (4)
H7	0.29 (2)	−0.168 (10)	0.777 (5)
H8	0.46 (3)	−0.12 (1)	0.653 (6)

positions of the hydrogen atoms were determined from a difference map.

A full-matrix least-squares refinement varying positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms reached convergence with $R = 0.037$, $R_w = 0.035$, and GOF = 1.36.[17] The final electron density difference map revealed no significant electron density greater than 0.41 e$^-$/Å^3. The crystal structure is shown in Figure 2 and atomic coordinates are given in Table II. Bond lengths and angles for **3A** and **3B** are given in Table III. Lists of observed and calculated structure factors and a table of anisotropic thermal parameters have been deposited as supplementary material.

Table III. Bond Lengths (Å) and Angles (deg)^b in **3A** and **3B**



	3A	**3B**		**3A**	**3B**
C(1)–C(2)	1.421	1.410	C(1)–O(1)	1.341	1.323
C(3)–C(4)	1.398	1.416	C(4)–O(4)	1.345	1.327
C(1)–C(1a)	1.384	1.406	C(9)–O(9)	1.236	1.234
C(4)–C(4a)	1.400	1.397	C(10)–O(10)	1.239	1.236
C(1a)–C(9)	1.466	1.459	C(2)–Cl(2)	1.721	1.721
C(4a)–C(10)	1.458	1.461	C(3)–Cl(3)	1.718	1.718
C(8a)–C(9)	1.473	1.482	C(2)–C(3)	1.376	1.368
C(5a)–C(10)	1.487	1.473	C(1a)–C(4a)	1.423	1.420
C(8a)–C(8)	1.395	1.395	C(5a)–C(8a)	1.391	1.397
C(5a)–C(5)	1.387	1.409	C(6)–C(7)	1.382	1.380
C(7)–C(8)	1.363	1.370	O(1)–H(1)	1.01	0.77
C(5)–C(6)	1.379	1.369	O(4)–H(4)	0.88	0.80
C(1a)–C(1)–C(2)	118.6	118.5	C(10)–C(4a)–C(1a)	120.9	120.5
C(4a)–C(4)–C(3)	119.3	119.0	C(1a)–C(9)–C(8a)	119.0	118.4
C(1a)–C(1)–O(1)	124.8	123.4	C(4a)–C(10)–C(5a)	118.5	118.2
C(4a)–C(4)–O(4)	123.5	123.1	C(1a)–C(9)–O(9)	120.8	121.0
C(2)–C(1)–O(1)	116.6	118.3	C(4a)–C(10)–O(10)	121.2	120.9
C(3)–C(4)–O(4)	117.2	117.9	C(8a)–C(9)–O(9)	120.2	120.6
C(1)–C(2)–C(3)	120.5	121.6	C(5a)–C(10)–O(10)	120.3	120.9
C(4)–C(3)–C(2)	121.3	120.6	C(9)–C(8a)–C(8)	120.0	120.3
C(1)–C(2)–Cl(2)	117.8	117.5	C(10)–C(5a)–C(5)	119.5	118.9
C(4)–C(3)–Cl(3)	118.8	117.7	C(9)–C(8a)–C(5a)	121.0	120.2
C(3)–C(2)–Cl(2)	121.7	120.9	C(10)–C(5a)–C(8a)	120.5	121.5
C(2)–C(3)–Cl(3)	119.9	121.7	C(8)–C(8a)–C(5a)	119.0	119.5
C(1)–C(1a)–C(9)	119.0	118.9	C(5)–C(5a)–C(8a)	119.9	119.6
C(4)–C(4a)–C(10)	119.7	119.3	C(8a)–C(8)–C(7)	120.5	120.0
C(1)–C(1a)–C(4a)	121.0	120.1	C(5a)–C(5)–C(6)	120.2	119.4
C(4)–C(4a)–C(1a)	119.3	120.2	C(8)–C(7)–C(6)	120.7	120.7
C(9)–C(1a)–C(4a)	119.9	120.9	C(5)–C(6)–C(7)	119.7	120.8

[a] The esds for C–O bonds are 0.006 Å, for C–C bonds 0.006–0.009, for C–Cl bonds 0.005, and for O–H bonds 0.05–0.07 Å. [b] The esds for bond angles involving only non-hydrogen atoms range from 0.4 to 0.6°.

Morphology of 3A. Crystals grown from chloroform at room temperature were orange six-sided prisms elongated on *b*. Major faces (Figure 3) were (001) and $(00\bar{1})$. End faces were (010) and $(0\bar{1}0)$, and the sides were formed by $\{\bar{1}02\}$ and $\{\bar{1}01\}$. In addition there were sometimes faces believed to be {211}, on the basis of the crystal packing together with measurement of the angle (50°) formed with the *b* axis (the long morphological axis) by their zone axis with major face (001).

Differentiation of 3A and 3B by X-ray Powder Photography. An X-ray powder photograph of a sample of **3A** grown by slow evaporation from chloroform at room temperature was markedly different from that of crystals of **3B** from a rapidly cooled solution of toluene (50–80 °C). A sample of **3A** heated above 140 °C gave a powder pattern similar to that of **3B** from warm toluene.

Differential scanning calorimetry of **3A** showed a very small broad endotherm whose exact position depended on the rate of heating but which developed in general between 130 and 190 °C. This was followed by a sharp melting endotherm at about 260 °C.

Observation of the Thermal Reaction of Single Crystals of 3A. When crystals of **3A** were heated on a microscope hot stage, examination showed that reaction began at one or more nucleation sites and spread

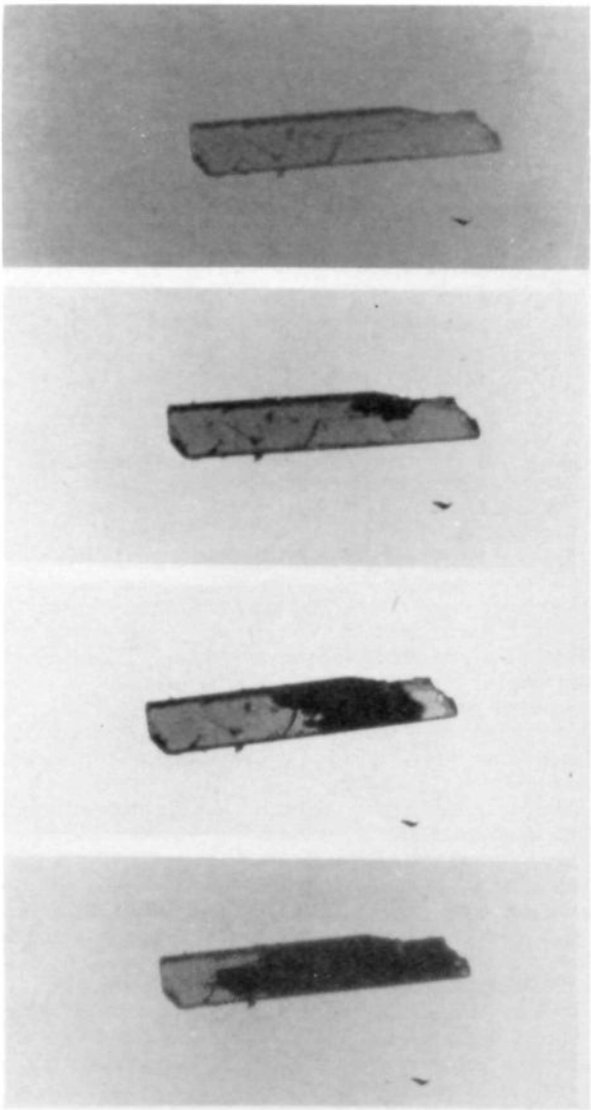


Figure 4. A crystal of **3A** heated at 132° and photographed after successive stages of reaction (top to bottom). Regions where reaction has occurred appear dark due to scattering of the light coming from the rear of the crystal. Note reaction begins in a small region and a reaction front spreads throughout the crystal.

through the crystal (Figure 4). Attempts to cause **3B** to revert to **3A** have thus far been unsuccessful. Samples submerged in liquid nitrogen for several days, or suspended in various agents such as Nujol or Fluorolube, remained unchanged as did samples left at room temperature for 3 years.

Use of Second Harmonic Generation To Follow the Rearrangement of 3A to 3B. Measurements[7] were made with a Molectron pulsed Nd^{3+} YAG laser (1064 nm) with Corion filters (756- and 532-nm cutoffs) and a Meret Inc. photomultiplier tube connected to a Tektronix 7834 storage oscilloscope. Samples employed were ungraded powders pressed between two microscope slides. Several samples of powder were compared to obtain an average value. Accuracy for this type of measurement has previously been estimated[7] as ±25% although it has been noted[18] that particle size and other factors may have an influence. No corrections were made for absorption or scattering. Since the absorption edge for quinizarins is approximately 550 nm and the second harmonic wavelength here is 532 nm, the true doubling efficiency could be considerably higher than we observed.[7] The transition from the centrosymmetric **3A** to the polar **3B** was followed by measurement of the detector voltage from the SHG produced by a sample of powdered **3A** heated at 2 deg/min.

Anisotropic Reaction of Crystalline Dichloroquinizarin 3 with Ammonia Gas. When single crystals of **3A** or **3B** were exposed to an atmosphere of ammonia gas for several hours an unstable violet colored polycrystalline complex was formed in agreement with the earlier report.[11] The ammonia complex retained the shape of the original crystal. Although indefinitely stable when stored in an ammonia atmosphere the complex, in the absence of ammonia, readily reverted to the original color as previously reported.[11]

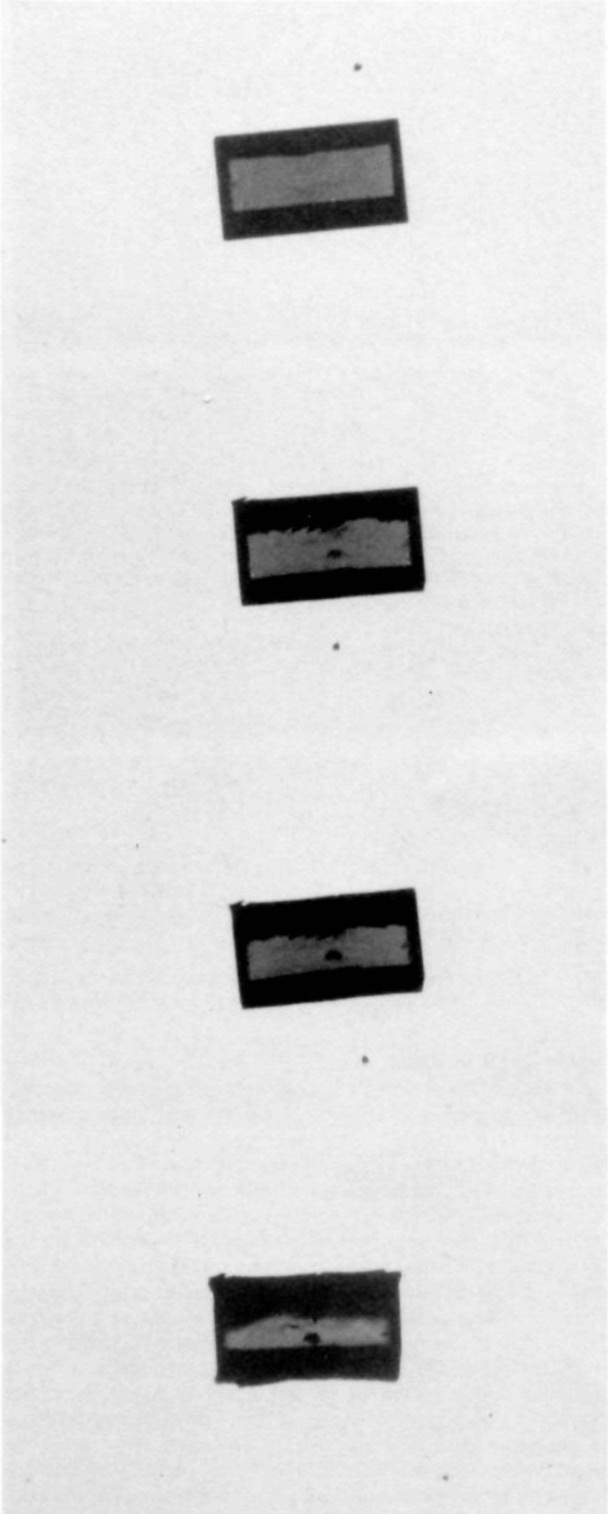


Figure 5. Crystal of **3A** undergoing reaction with ammonia gas. Orientation of the crystal is as in Figure 3a. Note that the preferred attack is on the {$\bar{1}02$} and {$\bar{1}01$} faces, where OH groups are exposed, rather than at the ends of the major (001) face of the crystal. Again the regions where reaction has occurred appear dark because the microcrystallites scatter light coming from the rear of the crystal.

The reaction of single crystals of **3A** with ammonia was highly anisotropic and began selectively at faces in the zones {101} and {102} as

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[18] Tweig, R. J.; Jain, K. Chapt 3, in ref 6a; see p 59.

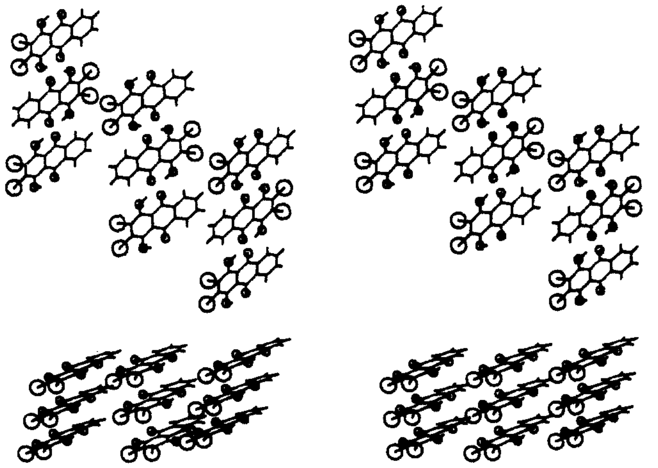

Figure 6. (a, top) Structure of **3A** showing the criss-crossed layers. The view is down *b* with *a* up in the plane of the page. The first chain goes in the [120] direction and the second along $[1\bar{2}0]$. (b, bottom) Structure of **3B** in an orientation selected to show the relationship of the structure to that of **3A**. Again the view is onto the (010) face (down *b*) but with *a* pointing down in the plane of the page. The two strips of molecules lie in the [110] and $[\bar{1}10]$ directions.

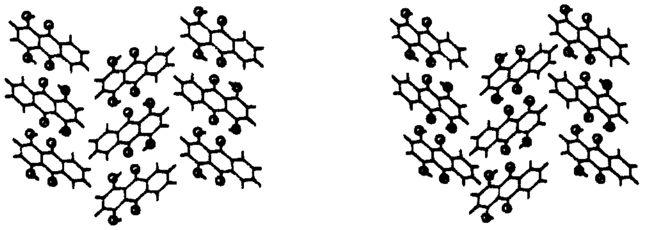

Figure 7. Structure[9] of unsubstituted quinizarin **2** in an orientation showing the resemblance to **3A**. View is down *c* with *b* vertical and a^* to the right in the plane of the page. The strips of molecules are parallel to $[0\bar{2}1]$ and [021].

shown in Figure 5 and spread in the *a* direction across the crystal. Migration of the reaction front both along *b* and along *c* was very significantly slower.

Results and Discussion

Crystals of **3A** undergo a change on heating above a temperature of approximately 130 °C as can be seen by microscopic observation of a single crystal (see Figure 4) or by differential scanning calorimetry. Although the product is microcrystalline, comparison of its infrared spectrum and X-ray powder photographs with those of **3B** prepared by crystallization from warm toluene confirms that they are identical. In order to show the nature of the change required for the conversion of **3A** to **3B** the two structures are presented in comparable orientations (Figure 6). The *molecular* structures in the two forms are essentially identical. The centrosymmetric structure **3A** is composed of strips in the [120] direction held together by hydrogen bonds. Adjacent molecules within a strip are related by crystallographic centers of symmetry. Operation of the *c*-glide plane on each strip produces an adjacent strip parallel to [120] and which criss-crosses the original strip. The remainder of the three-dimensional structure is built up by translation of these strips in the *b* and *c* directions. The structure of unsubstituted quinizarin **2** previously reported[9] is remarkably similar (Figure 7).

The polar structure (Figure 6) of **3B** may be viewed as being built up in a similar way from strips of molecules. In this case, however, the molecules forming a strip are related by translation and each strip is polar. Instead of hydrogen-bonded edge-to-edge contacts between adjacent molecules in a strip the molecules are rotated around an axis perpendicular to the molecular plane so that different closest contacts are involved. Molecules in a strip are slightly rotated out of the strip plane (the angle between the normal to the molecular plane and the [110] direction is about 94°) to give a slight stepping pattern not found in the strips of **3A**. However, the most important difference between the two structures in the present context is that the structure of **3B** is polar. As shown in Figure 6b both *a* and *c* axes are polar (all carbon–chlorine bonds point toward the left and somewhat toward the bottom of the page). (In space group *Pc* (class *m*) the only nonpolar directions are those parallel to the *b* axis.)[19] In addition a substantial component of the polarizable π system of the molecule is oriented along the *c* axis. The observed second harmonic generation by **3B** discussed in the Experimental Section (the intensity of the doubling is about twice that of urea) is thus consistent with the structure.

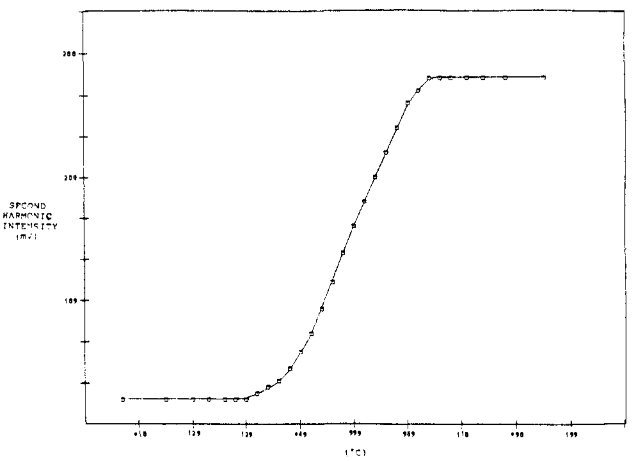

Figure 8. Plot of the second harmonic intensity (as measured by the output of the detector in mv) versus temperature when some crystals of **3A** are caused to rearrange to **3B** by heating.

There are remarkable similarities between the structural change in the transition of **3A** to **3B** with that in the previously reported[5] reversible interconversion of the room temperature form **1C** of naphthazarin C to the low-temperature form **1C′**. In each case the change in symmetry is from $2/m$ (space group $P2_1/c$) to *m* (space group *Pc*). The centrosymmetric structure **1C** is built up of centrosymmetric strips with adjacent molecules in a strip related by a center of symmetry as is **3A** above. The polar product **1C′** is built up from polar strips in a way similar to **3B** with those molecules forming a strip related only by translation. A previous publication[5a] shows structures of **1C** and **1C′** in orientations similar to those of **3A** and **3B** in Figure 6 above. There are of course major differences between these two centrosymmetric–polar interconversions. The naphthazarin rearrangement happens on cooling rather than heating, is readily reversible, and can be caused to occur as a single-crystal to single-crystal process. The naphthazarin transformation involves a larger change in molecular structure but a much smaller change in crystal packing.

That frequency doubling could be used to follow the rearrangement of centrosymmetric crystals of **3A** to microcrystalline **3B** on heating is shown in Figure 8. The important implications with regard to particle size and orientation in this kind of experiment have been discussed by Meredith and Williams and their collaborators.[20] In our experiment we have used a sample of small crystallites of **3A** with approximately random orientation. The product crystallites were therefore probably approximately randomly oriented. That the microcrystallites are of a particle size of 1000–10000 Å is suggested by the observation that a crystal heated and then placed in an X-ray powder camera without grinding gives a respectable powder photograph.[21] Since the wavelength of the incident laser beam was 1064 nm (10640 Å) it is reasonable that the particles had dimensions of the order of the wavelength of the radiation or larger. A single-crystal to single-crystal transition of a centrosymmetric to polar crystal would

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(19) See: Hahn, Th.; Klapper, H. *International Tables for Crystallography*; D. Reidel Publishing Co.: Dordrecht, 1983; Vol. A, pp 782 ff.

(20) See: Meredith, G. R.; Williams, D. J.; Fishman, S. N.; Goldburt, E. S.; Krongauz, V. A., In ref 6a, especially pp 144 ff.

(21) Brown, C. J. In *X-ray Diffraction of Polycrystalline Materials*; Peiser, H. S., Rooksby, H. P., Wilson, A. J. C., Eds.; Reinhold Publishing Corp. New York, 1960; p 399.

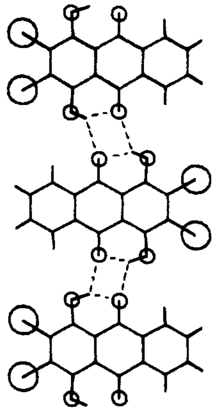

Figure 9. Hyrogen bonds between adjacent molecules of a strip in the structure of **3A**.

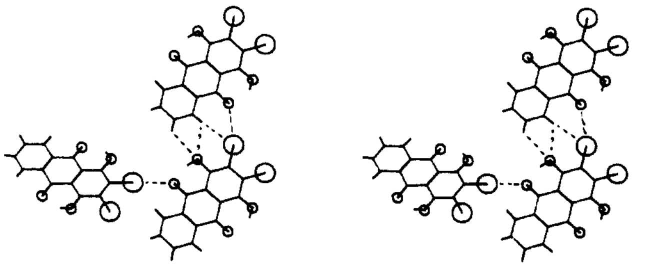

Figure 10. Intermolecular interactions between adjacent molecules in a strip of **3B** (upper and lower right) and between molecules in adjacent strips (lower left and lower right). In each case there are a number of weak interactions which seem to act cooperatively. Intermolecular distances (Å) from left to right are: Cl- - -O=C 3.13, HO- - -H 3.09, HO- - -H 3.00, H- - -Cl 3.08, and the Cl- - -O interaction between the two upper molecules has Cl- - -O=C 3.26 Å. The Cl—Cl- - -O angle = 166° and C=O- - -Cl = 140°.

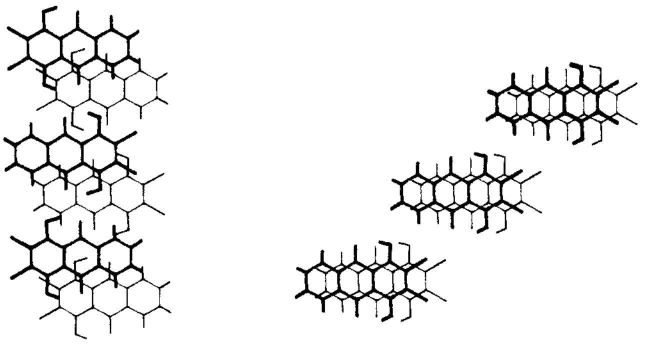

Figure 11. Difference in overlap in the structures of (left) 3A and (right) 3B.

be of interest. In this case there are two choices for the direction of orientation of the developing polar structure. The situation is similar to "spontaneous resolution"—development of a chiral crystal which can have either of two configurations with equal probability in the absence of any external bias. The solid-state resolution of crystalline binaphthyl, which undergoes a transition from a centrosymmetric to a chiral structure when heated, has been studied extensively, particularly by Pincock and Wilson.[22,23]

The nature of the intermolecular interactions in crystals of **3A** and **3B** deserves further comment. In the crystals of **3A**, and also in **2A**, there are strong intramolecular hydrogen bonds with bifurcation to adjacent molecules. The bifurcated hydrogen bonds binding the molecules in the strips of **3A** (or **2A**) form a motif (Figure 9) that has been observed previously in a variety of structures including salicylaldehyde,[24] tropolone,[25] dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate,[26] 1,4-bis(ethoxycarbonyl)-2,5-dihydroxy-1,4-cyclohexadiene,[27] and 2,4,6-trinitroaniline.[28]

The edge-to-edge interaction of molecules in strips found in **3B** is shown in Figure 10. The only hydrogen bonds in this structure are intramolecular; the edge-to-edge contacts are unlike those found in the structure of **3A**. Instead there are the loose Cl- - -O=C and C—H- - -OH contacts. In addition there might be mentioned a C—Cl- - -O=C interaction between molecules in adjacent stacks of **3B** (Figure 10).

A major difference in the packings of polymorphs **3A** and **3B** is the overlap between molecules in adjacent layers as shown in Figure 11. The overlap in **3A** is rather similar to that in naphthazarin A with the molecular axes of adjacent molecules parallel.[5] The overlap in **3B** is different, not only from that in **3A** but also from that in any of the unsubstituted naphthazarins.

An aspect of the transition of **3A** to **3B** which requires comment has been our failure to observe the reverse process. The cell constants obtained from the two structures determined at room temperature suggest that **3B** is slightly more dense than **3A**. In contrast, the unchlorinated quinizarin **2A** on heating undergoes a change to a second form **2B** which has a slight increase in the volume per molecule calculated from the cell constants reported by Borgen,[10] who reported also that crystals of **2B** reverted spontaneously to **2A** at room temperature. Comparison of the cell constants of **2B** with those of **3B** suggests the possibility that the structures are similar.

Bond lengths and angles for **3A** and **3B** are given in Table III. The structures of the molecules making up the two forms of **3** are very similar. In both forms, the molecule closely approaches C_{2v} symmetry. Spectral studies have led to the proposal[29] that in solution quinizarin is a mixture of 9,10- and 1,4-diketo tautomers in rapid equilibrium as is true of naphthazarins, even in the crystalline state.[5] However, the central rings of the dichloroquinizarins **3A** and **3B** show the geometry to be expected of a quinonoid ring with the hydroxylic hydrogen atoms bonded to O_1 and O_2 of the adjacent rings, as has been the case in all other quinizarin derivatives thus far studied. Thus, lengths of C_1–O_1 and C_4–O_4 are 1.323 (6)–1.345 (6) Å, typical of phenolic C–O single bonds,[30] while lengths of C_9=O_9 and C_{10}=O_{10} are 1.234 (6)–1.239 (6) Å, similar to those of anthraquinone.[31] The entire ring system closely approaches planarity with dihedral angles between adjacent planes in the range of 1.8–2.9°.

In the crystal of **3A**, the intramolecular O(1)- - -O(9) and O(4)- - -O(10) distances are 2.566 (5) and 2.576 (5) Å, respectively; the corresponding H- - -O contacts are 1.67 (7) and 1.81 (5)°, and the O—H- - -O angles are 146 (6) and 145 (5)°. In **3B**, the intramolecular O(1)- - -O(9) and O(4)- - -O(10) distances are 2.545 (6) and 2.546 (5) Å, while the corresponding H- - -O contacts are 1.88 (7) and 1.79 (10) Å, with O—H- - -O angles of 143 (7) and 150 (9)°. As 2,3-dichloroquinzarin is involved in bifurcated intermolecular hydrogen bonding only in the crystal of **3A**, it is of interest to note significantly longer O- - -O intramolecular distances in that crystal as compared to **3B**. The *inter*molecular O(1)- - -O(9) and O(4)- - -O(10) distances in **3A** are 2.898 and 3.006 Å, respectively.

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Supplementary Material Available: Tables of thermal parameters for the two polymorphs of 2,3-dichloroquinizarin (3A and 3B) (2 pages); listings of observed and calculated structure factors for the two polymorphs of 2,3-dichloroquinizarin (**3A** and **3B**) (11 pages). Ordering information is given on any current masthead page.

Ascorbic Acid Photoreductions of Zinc(II) Chlorophyll Derivatives: Access to Metal-Free Isobacteriochlorins

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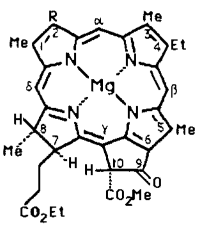
Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received October 30, 1987*

Abstract: The products and resultant stereochemistry of the ascorbic acid/organic base photoreduction of zinc(II) chlorins were investigated. In the pheophorbide series the reaction is shown to give a *cis*-isobacteriochlorin **15** with a vinyl group external to the newly reduced ring. It is further demonstrated that under the basic reaction conditions this vinyl group is prone to double-bond migration toward the ring to give a stable ethylideneisobacteriochlorin **10**. The biological implications of formation of the ethylidene moiety in this fashion are discussed. In addition, substituents were found to have a pronounced effect on the regiochemical selectivity of the reaction, as demonstrated by reduction of two rhodochlorin derivatives of methyl pheophorbide *a*. Demetalation of appropriate zinc(II) complexes yields the metal-free isobacteriochlorins **11**, **13**, and **15a**.

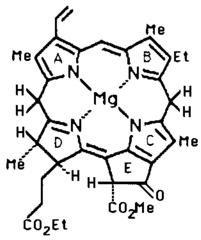
The ascorbic acid photoreduction of metalloporphyrins (to give chlorins) and metallochlorins (to give isobacteriochlorins) and the associated mechanistic pathways have been extensively investigated.[1-6] Originally, the interest in this area was focused on the possible relationship of this chemical reduction route to the biosynthetic formation of chlorophyll *a* from protochlorophyll. Early investigations[3,4] examined the roles of the organic base (e.g., pyridine) and the activator (ethanol or water), which were both necessary to afford reduction, and suggested that the base and ascorbate complexed to form the active reductant, which then reacted with the photoexcited metalloporphyrin or metallochlorin. The Lewis acid, which was also necessary, acts as a proton source. The product of chlorophyll *a*/ascorbic acid photoreduction, characterized by its unusual optical spectrum, is a pink compound (λ_{max} 525 nm), the formation of which can be reversed by oxygen or dehydroascorbic acid.

The structure of the ethyl chlorophyllide *a* (**1**, Chart I) photoreduction product was originally proposed to be the porphodimethene **2** by Krasnovski in 1948[5] and later confirmed by Scheer and Katz,[6] who monitored the photoreduction of chlorophyll *a* in pyridine-d_5 and hydrogen sulfide by proton NMR spectroscopy. However, prior to this structural determination, Seely demonstrated[7] that under specific conditions, photoreduction of **1** gives a stable tetrahydroporphyrin, which results from the rearrangement of the porphodimethene under light or dark conditions. The structural evidence in this report was based on a series of spectrophotometric experiments by Seely, who cleverly deduced the correct ring structure of the stable tetrahydroporphyrin.

Chart I



1 R = CH=CH$_2$
4 R = Et



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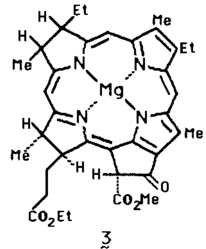

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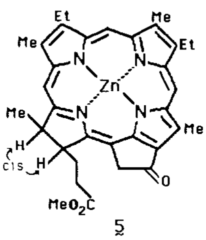

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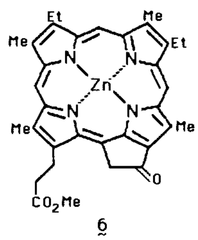

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Primarily on the basis of interpretation of the blue-shifted band (626 nm) and on oxidation studies of the reduced products, Seely proposed the tetrahydroporphyrin **3** as the end product of the ascorbate photoreduction. The reduced product, upon oxidation with different quinone oxidants, gave optical spectra similar to those of mesochlorophyllide *a* (**4**).[7] Thus it was postulated that the vinyl group was in some way reduced during the course of

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