Table 3. *Selected structural parameters for the phosphate esters* (3), (2*a*)–(2*e*)

	(3)*	(2*a*)	(2*b*)	(2*c*)	(2*d*)	(2*e*)
A. Ring torsion angles (°, absolute values)						
C(6)–O(1)–P–O(3)	45·2 (6)	41·1 (3)	38·7 (2)	44·7 (3)	40·4 (3)	38·5 (3)
O(1)–P–O(3)–O(4)	44·0 (6)	41·3 (3)	38·9 (2)	46·6 (3)	41·0 (3)	40·2 (3)
P–O(3)–C(4)–C(5)	53·4 (6)	52·0 (4)	50·7 (3)	54·3 (3)	50·6 (3)	52·1 (3)
O(3)–C(4)–C(5)–C(6)	56·5 (6)	57·1 (4)	58·9 (3)	55·4 (4)	56·4 (4)	59·1 (3)
C(4)–C(5)–C(6)–O(1)	57·6 (6)	56·5 (4)	58·6 (3)	53·9 (4)	55·5 (4)	57·6 (3)
C(5)–C(6)–O(1)–P	55·1 (6)	50·7 (3)	50·2 (3)	50·9 (3)	49·1 (3)	48·9 (3)
B. Bond and torsion angles at phosphorus (°)						
C(6)–O(1)–P	118·0 (3)	119·4 (2)	118·9 (2)	118·2 (2)	119·0 (3)	119·3 (2)
O(1)–P–O(3)	105·7 (2)	106·7 (2)	107·5 (2)	105·9 (2)	107·7 (2)	107·6 (2)
P–O(3)–C(4)	118·0 (3)	118·8 (3)	118·0 (2)	117·9 (2)	118·6 (3)	118·5 (2)
O(1)–P–O(2)	101·7 (3)	106·8 (2)	105·5 (2)	100·7 (2)	105·4 (2)	105·5 (2)
O(3)–P–O(4)	111·1 (2)	114·9 (2)	114·6 (2)	113·2 (2)	113·8 (2)	114·6 (2)
O(2)–P–O(4)	116·0 (2)	113·9 (2)	114·0 (2)	115·0 (2)	114·6 (2)	114·6 (2)
P–O(2)–C(11)	122·5 (4)	120·6 (2)	120·4 (2)	124·3 (2)	124·7 (2)	129·0 (2)
O(1)–P–O(2)–C(11)		67·7 (3)	72·3 (2)	160·4 (2)	−56·4 (3)	74·5 (2)
O(3)–P–O(2)–C(11)		179·0 (3)	−175·9 (2)	−89·6 (2)	−168·6 (3)	−174·1 (2)
O(4)–P–O(2)–C(11)		−57·4 (3)	−52·4 (2)	35·9 (3)	68·5 (3)	−51·5 (3)
P–O(2)–C(11)–C(12)		73·8 (3)	75·7 (3)	−125·3 (3)	140·9 (3)	−154·7 (2)
C. Bond lengths (Å)						
P–O(2)	1·565 (4)	1·587 (3)	1·594 (2)	1·597 (3)	1·600 (2)	1·599 (2)
P–O(1)	1·567 (4)	1·549 (3)	1·559 (2)	1·550 (3)	1·542 (3)	1·547 (2)
P–O(3)	1·565 (4)	1·547 (3)	1·559 (2)	1·551 (2)	1·550 (3)	1·557 (2)
P–O(4)	1·444 (4)	1·458 (3)	1·458 (2)	1·447 (3)	1·449 (3)	1·445 (2)
C(6)–O(1)	1·450 (6)	1·453 (4)	1·467 (4)	1·467 (4)	1·476 (4)	1·473 (3)
C(4)–O(3)	1·472 (6)	1·462 (5)	1·461 (3)	1·455 (4)	1·468 (4)	1·472 (3)
C(11)–O(2)	1·428 (6)	1·408 (3)	1·400 (3)	1·383 (3)	1·376 (4)	1·368 (3)

* van Nuffel, Lenstra & Geise (1980).

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Acta Cryst. (1984). C**40**, 1065–1068

Laser Dye Intermediates: Structures of 1,2,3,4-Tetrahydroquinolinium-7-sulfonate Monohydrate (I), $C_9H_{11}NO_3S.H_2O$, and Twinned 1,2,3,4-Tetrahydro-1-methylquinolinium-7-sulfonate (II), $C_{10}H_{13}NO_3S$

By Judith L. Flippen-Anderson and Richard Gilardi

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, *USA*

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Abstract. (I): $M_r = 231{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}979\ (4)$, $b = 9{\cdot}096\ (6)$, $c = 14{\cdot}492\ (6)$ Å, $\beta = 96{\cdot}03\ (4)^\circ$, $F(000) = 488$, $V = 1046{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ Mg m^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 2{\cdot}9$ mm^{-1}, $T = 295$ K, final $R = 0{\cdot}057$ for 1374 unique reflections. (II): $M_r = 227{\cdot}3$, monoclinic, $P2_1/n$, $a = 9{\cdot}343\ (4)$, $b = 14{\cdot}235\ (6)$, $c = 7{\cdot}706\ (4)$ Å, $\beta = 95{\cdot}71\ (4)^\circ$, $F(000) = 480$, $V = 1019{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}48$ Mg m^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 2{\cdot}89$ mm^{-1}, $T = 295$ K, final $R = 0{\cdot}069$ for 1140 unique reflections. Crystals of (II) were found to be twinned, with components of the twin present in approximately equal amounts. The X-ray results showed the sulfonyl group to be in the *meta* position with respect to the quinoline moiety. Both (I) and (II) are zwitterions in the crystalline phases studied.

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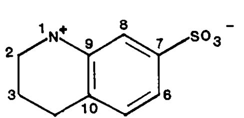
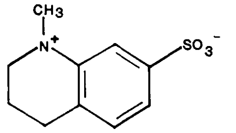
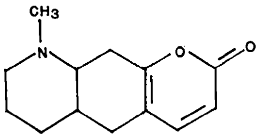
Introduction. Efficient and stable lasing dyes emitting around 480 nm are of interest for dye laser sources to be used in underwater experiments. Several coumarin derivatives [*e.g.* (I), (II), (III) and (IV)] lase efficiently in this region (Schimitschek, Trias, Hammond, Henry & Atkins, 1976). Many of these dyes have commercial applicability if they can be produced cheaply in ton quantities. For the dye-preparation procedure to be thoroughly characterized it is necessary to identify unequivocably all intermediate products. Two of these intermediates were purified, crystallized, and sent to us by Dr P. R. Hammond of the Lawrence Livermore Laboratories (Livermore, California); the diffraction analysis of these crystals definitely showed that their structures are as shown in (I) and (II).



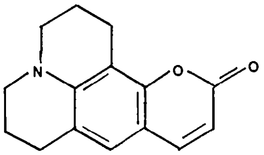
(I)



(II)



(III)



(IV)

Experimental. For (I) [where different, values for (II) in square brackets]: unit-cell parameters from least-squares analysis of 20 [25] reflections with 2θ from 18 to 35° [27 to 35°], $P2_1/c$ [$P2_1/n$] derived from systematic absences, 1374 [1344] independent reflections with $2\theta_{max} = 45°$; three standard reflections measured after every 60 new reflections showed an average random variation of 2·4% [2·0%] in $|F_o|$. For both crystals: D_m not determined, Nicolet P3F automatic diffractometer, θ:2θ scanning mode with variable scan rate, Lorentz–polarization corrections, no absorption or extinction corrections. Both structures solved by direct methods (Karle & Karle, 1966) as implemented by the *MULTAN*80 system of computer programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). For both molecules the function minimized by least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. Weights, w, calculated based on counting statistics with a term added (0·02) for random instrumental errors as described by Gilardi (1973). Molecule (I) was refined by restrained least squares [non-H atoms anisotropic, H atoms (from difference map) riding on bonded atoms] using program *RESLSQ* (Flippen-Anderson, Gilardi & Konnert, 1983) and all 1374 reflections to a final R factor of 0·057 (R_w = 0·050, S = 1·3). $(\Delta/\sigma)_{max} = 0{\cdot}52$. Max. height in final difference synthesis 0·40 e Å^{-3}. Molecule (II) was refined by full-matrix least squares [non-H atoms anisotropic, H atoms (from difference map) given constant isotropic B's set at value for covalently bonded atoms] using program *ORXFLS*3 (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1975) and 1140 reflections (see discussion on twinning) to a final R factor of 0·069 (R_w = 0·064, S = 1·6). $(\Delta/\sigma)_{max} = 0{\cdot}81$. Max. height in final difference synthesis 0·32 e Å^{-3}.

Twinning of crystal (II)

The automatic indexing programs for the diffractometer indicated an orthorhombic cell with fairly long a axis (37·2 Å). The lattice was very sparsely occupied and appeared to have general extinctions which corresponded to no standard orthorhombic space group. Careful inspection of this diffraction pattern revealed that the crystals of (II) were actually monoclinic, but were twinned on $h00$ with effectively equal diffracting volumes for the individual components. As shown in Fig. 1, layers with $l = 4n$ are composed of reflections which overlap. An ideal interpretation of the pattern illustrated in Fig. 1 implies a geometric relationship which can be expressed in terms of parameters of the real cell:

$$c + 8a\cos\beta = 0. \qquad (1)$$

From the measured cell parameters and their e.s.d.'s an experimental measurement of this quantity is found to be

$$c + 8a\cos\beta = 0{\cdot}27 \pm 0{\cdot}05 \text{ Å}, \qquad (2)$$

showing that the overlap is very close but may not be exact. However, calculation of the diffractometer settings for each of the components indicated that reflections would not be resolvable on the overlapped layers.

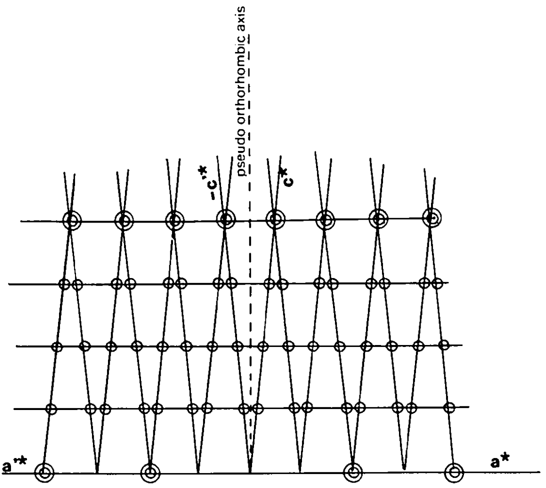


Fig. 1. The superimposed a^*c^* nets of the twinned quinoline (II). Overlapped layers are indicated with double circles.

Table 1. *Fractional coordinates and B_{eq} values for molecule* (I)

Standard deviations, given in parentheses, are based solely on least-squares results. $B_{\text{eq}} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where the β_{ij} values are the final refined anisotropic thermal parameters.

	x	y	z	B_{eq}(Å^2)
N(1)	0·8393 (3)	0·7553 (3)	0·6012 (2)	3·0 (1)
C(2)	0·8822 (5)	0·8498 (4)	0·5221 (3)	3·8 (1)
C(3)	0·7466 (5)	0·8359 (5)	0·4418 (3)	4·1 (1)
C(4)	0·7370 (4)	0·6790 (4)	0·4066 (2)	3·7 (1)
C(5)	0·6975 (4)	0·4221 (4)	0·4652 (2)	3·2 (1)
C(6)	0·7065 (4)	0·3161 (4)	0·5340 (2)	3·0 (1)
C(7)	0·7640 (4)	0·3560 (4)	0·6249 (2)	2·5 (1)
C(8)	0·8084 (4)	0·4993 (4)	0·6462 (2)	2·6 (1)
C(9)	0·7964 (4)	0·6028 (4)	0·5755 (2)	2·5 (1)
C(10)	0·7440 (4)	0·5674 (4)	0·4840 (2)	2·7 (1)
S(11)	0·7815 (1)	0·2185 (1)	0·7127 (1)	2·9 (1)
O(12)	0·8543 (4)	0·2910 (3)	0·7965 (2)	5·0 (2)
O(13)	0·6119 (3)	0·1670 (3)	0·7212 (2)	4·1 (1)
O(14)	0·8879 (3)	0·1045 (3)	0·6814 (2)	5·6 (2)
Water	0·4478 (5)	0·1271 (4)	0·3435 (3)	4·7 (2)

Table 2. *Fractional coordinates and B_{eq} values for molecule* (II)

Standard deviations, given in parentheses, are based solely on least-squares results. $B_{\text{eq}} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$, where the β_{ij} values are the final refined anisotropic thermal parameters.

	x	y	z	B_{eq}(Å^2)
N(1)	1·2690 (4)	0·3734 (3)	0·1992 (6)	2·5 (1)
C(2)	1·3577 (7)	0·4503 (4)	0·1235 (9)	3·3 (2)
C(3)	1·3469 (7)	0·5405 (5)	0·2271 (10)	4·2 (2)
C(4)	1·1929 (8)	0·5745 (4)	0·2096 (10)	3·5 (2)
C(5)	0·9471 (6)	0·5178 (4)	0·2758 (9)	3·1 (2)
C(6)	0·8475 (6)	0·4477 (4)	0·2964 (8)	3·1 (2)
C(7)	0·8872 (5)	0·3544 (4)	0·2816 (7)	2·4 (1)
C(8)	1·0246 (5)	0·3310 (4)	0·2494 (8)	2·4 (1)
C(9)	1·1225 (5)	0·4025 (4)	0·2298 (7)	2·3 (1)
C(10)	1·0868 (6)	0·4969 (4)	0·2405 (8)	2·7 (1)
S(11)	0·7569 (1)	0·2637 (1)	0·2959 (2)	2·8 (0)
O(12)	0·8304 (4)	0·1754 (3)	0·2761 (6)	3·3 (1)
O(13)	0·7090 (4)	0·2728 (3)	0·4708 (6)	3·5 (1)
O(14)	0·6439 (4)	0·2841 (3)	0·1588 (6)	3·9 (1)
C(15)	1·3476 (7)	0·3328 (5)	0·3648 (10)	3·8 (2)

Table 3. *Comparison of bond lengths* (Å) *and bond angles* (°) *for* (I) *and* (II)

	(I)	(II)
N(1)–C(2)	1·500	1·524
N(1)–C(9)	1·467	1·471
N(1)–C(15)		1·522
C(2)–C(3)	1·514	1·521
C(3)–C(4)	1·515	1·511
C(4)–C(10)	1·509	1·518
C(5)–C(6)	1·382	1·384
C(5)–C(10)	1·392	1·392
C(6)–C(7)	1·396	1·386
C(7)–C(8)	1·377	1·373
C(7)–S(11)	1·780	1·786
C(8)–C(9)	1·387	1·387
C(9)–C(10)	1·386	1·389
S(11)–O(12)	1·448	1·448
S(11)–O(13)	1·449	1·467
S(11)–O(14)	1·444	1·447

	(I)	(II)
C(2)–N(1)–C(9)	114·5	114·1
C(2)–N(1)–C(15)		111·0
C(9)–N(1)–C(15)		110·6
N(1)–C(2)–C(3)	109·6	109·8
C(2)–C(3)–C(4)	110·0	109·6
C(3)–C(4)–C(10)	112·8	112·6
C(10)–C(5)–C(6)	122·0	121·5
C(5)–C(6)–C(7)	119·0	119·5
C(6)–C(7)–C(8)	120·6	120·7
C(6)–C(7)–S(11)	119·0	119·9
C(8)–C(7)–S(11)	120·4	119·4
C(7)–C(8)–C(9)	118·7	118·7
C(8)–C(9)–N(1)	117·3	116·4
C(8)–C(9)–C(10)	122·7	122·6
C(10)–C(9)–N(1)	120·1	120·0
C(4)–C(10)–C(5)	120·4	121·0
C(4)–C(10)–C(9)	122·6	122·0
C(5)–C(10)–C(9)	117·0	117·0
C(7)–S(11)–O(12)	105·9	106·8
C(7)–S(11)–O(13)	106·5	105·4
C(7)–S(11)–O(14)	106·5	105·2
O(12)–S(11)–O(13)	111·9	111·4
O(12)–S(11)–O(14)	113·2	114·6
O(13)–S(11)–O(14)	112·3	112·7

Once the twinning was resolved it was possible to index each reflection on a monoclinic lattice belonging to one twin or the other and then select reflections from a single twin for diffractometer alignment and subsequent data collection. The extinctions for this set of data indicated space group $P2_1/n$. The overlapping reflections on the zero ($l = 0$) layer had the same or symmetry-equivalent indices while those overlapping on the $l = 4n$ layers did not. Therefore, for refinement purposes the $l = 0$ data were put on a separate scale factor and the $l = 4n$ (204 reflections) data omitted.

Discussion. Final refined coordinates are given in Tables 1 and 2 for molecules (I) and (II), respectively.* The results of the X-ray analyses on (I) and (II) are shown in Fig. 2. Distances and angles for the two molecules are compared in Table 3. Standard deviations in these values, based solely on the least-squares results, are 0·006 Å for bond lengths and 0·4° for bond angles in (I) [0·008 Å and 0·5° in (II)]. In both molecules the e.s.d.'s involving the S atom are 0·004 Å for bond lengths and 0·3° for bond angles. Both distances and angles agree quite well between the two structures with only the N(1)–C(2) and S(11)–O(13) bond lengths differing by more than 3σ. The conformations of both molecules are also essentially the same. The aromatic rings are planar [average absolute value of ring torsion is 1·1° for (I) and 0·8° for (II)]. The saturated rings are in a half-chair conformation with C(2) and C(3) twisted out of the plane of the other four ring atoms. Unit-cell

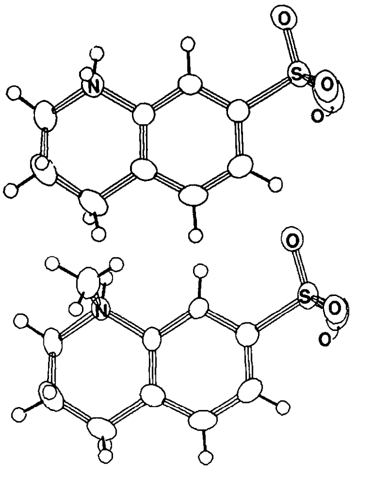


Fig. 2. The results of the X-ray study on (I) (top) and (II) (bottom) drawn using the program *ORTEP* (Johnson, 1965) with the thermal parameters at the 50% probability level.

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* Lists of structure factors, anisotropic thermal parameters for the non-H atoms and coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39256 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor (*X*)	Acceptor (O)	*X*···O	*X*–H	H···O	*X*–H···O
Molecule (I)					
N(1)	O(12)	2·743 (6)	0·92 (7)	1·87 (7)	156 (6)
N(1)	H_2O	2·724 (7)	0·93 (7)	1·80 (7)	170 (5)
H_2O	O(13)	2·976 (7)	0·88 (7)	2·10 (7)	171 (6)
H_2O	O(13)	2·858 (6)	0·89 (7)	1·98 (7)	170 (6)
Molecule (II)					
N(1)	O(13)	2·746 (6)	0·99 (7)	1·76 (7)	169 (6)

packing is influenced by hydrogen bonding. In both molecules all available H atoms participate in intermolecular hydrogen bonds (parameters are given in Table 4). In (I) water crystallized with the quinoline. The H_2O acts as a donor in hydrogen bonds to two different O(13) atoms and as an acceptor from one of the H atoms on N(1). The remaining H on N(1) acts as a donor to O(12). In addition to the hydrogen bonds there is one intermolecular approach less than van der Waals distances, C(2)···C(2) at 3·42 Å. In (II) there is only one H available for hydrogen bonding and it acts as a donor to O(13). There are no other approaches in (II) which are less than van der Waals separations.

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A Structure Containing Diastereomers, (2*S*,4*R*)-*trans*- and (2*R*,4*R*)-*cis*-2-Hydroxy-2,4-dimethyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one, $C_{14}H_{14}O_4$

By Edward J. Valente* and Verner Schomaker

Department of Chemistry, University of Washington, Seattle, Washington 98195, *USA*

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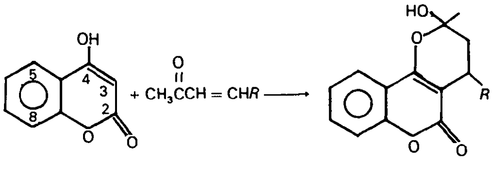
Abstract. $M_r = 246{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}804\ (3)$, $b = 18{\cdot}248\ (8)$, $c = 8{\cdot}752\ (5)$ Å, $\beta = 99{\cdot}59°$, $V = 1233$ Å^3, $Z = 4$ (2 molecules/asymmetric unit), $D_x = 1{\cdot}33$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71067$ Å, $\mu = 0{\cdot}91$ cm^{-1}, $F(000) = 520$, $T = 293$ K. Final $R = 0{\cdot}066$ for 1123 observed independent intensities. The structure consists of diastereomers approximately inversion-related through a pseudocenter of symmetry at $x = 0{\cdot}241\ (4)$, $z = 0{\cdot}281\ (3)$ except the 4-methyl groups. The dihydropyran rings are half chairs distorted towards the *e,f*-diplanar conformation. Like molecules are hydrogen-bonded between hydroxyl and carbonyl groups along **a**, O···O distances being 2·781 (7) (*trans*) and 2·780 (7) Å (*cis*).

Introduction. Michael-type addition of certain α,β-unsaturated ketones with 4-hydroxycoumarin leads to 3-substituted 4-hydroxycoumarins. In solution these products exist in a dynamic equilibrium between diastereomeric hemiketals and the open (keto) form of the molecule. The compound so obtained using 3-penten-2-one ($R = CH_3$) consists of about equal parts of each isomer in chloroform solution (Valente, Santarsiero & Schomaker, 1979), and its crystalline racemate consists of *cis* diastereomeric forms. As part of a structural study of this Michael addition product, we resolved the optical isomers and undertook a crystallographic investigation. In crystallizing the compound under different conditions, we hoped to observe another of the isomeric forms apparently present in solution.



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[*] Current address: Department of Chemistry, Mississippi College, Clinton, MS 39058, USA.

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