

## The Molecular and Crystal Structure of 6-Methoxy-8-Nitro-5(1*H*)-Quinolone and its Dielectric Properties

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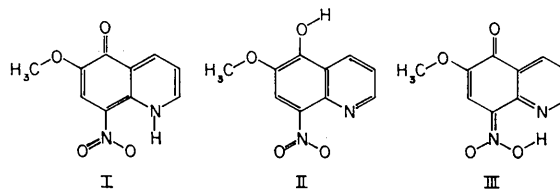
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A crystalline substance that was assumed on chemical grounds to be 5-hydroxy-6-methoxy-8-nitroquinoline is shown by a three-dimensional X-ray analysis to consist predominantly of 6-methoxy-8-nitro-5(1*H*)-quinolone (I), although the presence in small concentrations of the 5-hydroxy and acinitro tautomers could not be ruled out. The crystals are orthorhombic and the space group is *Pca*2<sub>1</sub>. The unit-cell dimensions are  $a = 18.647 \pm 0.006$ ,  $b = 6.363 \pm 0.003$  and  $c = 7.730 \pm 0.003$  Å.  $V = 917$  Å<sup>3</sup>,  $Z = 4$  and  $D_m = 1.62$  g.cm<sup>-3</sup>. The conventional *R* value based on 829 structure factors is 0.051. The structure contains a bifurcated hydrogen bond wherein the hydrogen atom attached to the quinoline nitrogen is hydrogen bonded intermolecularly to the oxo group and intramolecularly to one of the nitro oxygen atoms. An extraordinarily short C-N distance, 1.404 Å, is observed between C(8) of the quinoline ring and the nitro group, which deviates by only 7° from coplanarity with the ring. Dielectric and tangent loss measurements on powder samples indicated that conversion of (I) to a tautomeric form, through a proton transfer induced by the applied electric field, is not evident within the range of frequencies from 50 to 10<sup>10</sup> Hz.

### Introduction

The difference in color between the brick red crystals of the compound which Elderfield (1946) designated as 5-hydroxy-6-methoxy-8-nitroquinoline (II) and the nearly colorless crystals of 5-acetoxy-6-methoxy-8-nitroquinoline seemed irreconcilable with the similarity in the structural formulas proposed for these molecules. This apparent anomaly led us to speculate that a greater diverseness exists in their molecular structures than merely the substitution of an acetoxy by a hydroxy group. In order to compare the stereochemical details of these molecules, the crystal structures of both compounds were determined. The results of the analysis of the acetoxy compound have been reported previously (Sax & Desiderato, 1967). The crystal structure of the unesterified compound is considered in this paper. The unusual solubility of the red compound cast further doubt upon the validity of assuming structural formula (II) for this compound. For instance, although it is insoluble in most of the usual solvents at room temperature, it dissolves easily in 18*N* sulfuric acid to yield a pale yellow solution from which red crystals are grown by careful dilution with water. This reaction suggests that the red form is either the cross conjugated tautomer (I) or the acinitro compound (III), which transforms into the enolic form on dissolving in sulfuric acid. Our analysis shows that the molecules in the red

crystals are predominantly (I), although the tautomeric forms (II) and (III) may be present also in lower concentrations. Dielectric constant measurements were made on the red crystals to see if interconversion of the tautomers could be induced by an applied electric field.



### Experimental

#### *X-ray diffraction*

Single crystals of 6-methoxy-8-nitro-5(1*H*)-quinolone (I), C<sub>10</sub>H<sub>18</sub>O<sub>4</sub>N<sub>2</sub>, were prepared for us by Dr S. M. Sax. The compound crystallizes in the orthorhombic system. From the systematic absences, *0kl* with *l* odd and *h0l* with *h* odd, the possible space groups are *Pcam* and *Pca*2<sub>1</sub>. The latter space group was chosen to avoid a disordered model as would have been required in *Pcam*. The unit-cell dimensions and their estimated standard deviations were obtained from 2θ measurements of axial reflections that were made on a Picker full-circle diffractometer using Cu *K*α radiation ( $\lambda = 1.5418$ ,  $\alpha_1 = 1.5405$ ,  $\alpha_2 = 1.5443$  Å). They are as follows  $a = 18.647 \pm 0.006$ ,  $b = 6.363 \pm 0.003$ ,  $c = 7.730 \pm$

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0.003 Å.  $Z=4$ .  $D_m=1.62$  g.cm<sup>-3</sup> by the flotation method.  $D_x=1.595$  g.cm<sup>-3</sup>. M.W. 220.164.  $V=917$  Å<sup>3</sup>.

Both diffractometer and photographic data were collected using Cu  $K\alpha$  radiation. Eight hundred twenty five independent reflections were measured in the  $\sin \theta$  range 0.083 through 0.899 on a Picker full-circle automated diffractometer. The crystallographic  $c$  axis was set to coincide with the  $\varphi$  axis. An additional six levels of photographic data were collected on multifilm equi-inclination Weissenberg photographs from a crystal rotated about the  $c$  axis. These intensities were measured visually by comparison with a calibrated film strip. They were scaled to the diffractometer data by a least-squares method after reduction to structure factor magnitudes. The photographic data used in the analysis were limited to 113 reflections that fell in the  $\sin \theta$  range 0.833 to 0.989 and were not measured on the diffractometer. Spot shape corrections (Phillips, 1956) were applied to the Weissenberg data. No corrections were made for absorption or extinction.

### Structure determination and refinement

It was clearly evident from inspecting a three-dimensional  $E^2$ -Patterson synthesis that the fused ring must be tilted relative to the  $ab$  plane. If  $Pcam$  were assumed as the space group, then with four molecules in the unit cell, this feature of the molecular packing would require disordering of the atoms across a mirror plane, since this is the point symmetry of the only special position in  $Pcam$  that is consistent with the observed systematic absences. Accordingly  $Pca2_1$  was chosen for the structure determination. Although the interpretation by inspection of the Patterson function was complicated by the presence of a dominant hexagonal subcell, the structure was found straightforwardly by Patterson superposition methods (Buerger, 1959) which have been programmed for the IBM 1620 computer (Corfield, 1965). Initially the location in the unit cell of a hexagonal moiety of the fused ring was obtained from a '6-atom Symmetry Minimum Function' (Corfield & Rosenstein, 1966). Then a 24-atom multiple minimum function based upon the six-membered ring and its symmetry equivalents yielded twelve of the sixteen non-hydrogen atoms. The remaining four atoms were located in a three-dimensional difference Fourier synthesis phased on these twelve atoms and containing 183 terms with  $|F_c| \geq |F_o|$ . At this stage of the analysis, the conventional  $R$  index, calculated with a single overall temperature factor, was 0.34 for the diffractometer data.

The structure was refined by full matrix least-squares (Busing, Martin & Levy, 1962) using only the diffractometer data initially. The  $z$  coordinate of N(1) was fixed during the entire refinement, and the quantity minimized was  $\sum w(F_o - KF_c)^2$ . The weighting scheme was that of Hughes (1941) with  $4F_{\min}$  equal to 8. Several very weak reflections and some that appeared to be affected significantly by systematic error were given zero weight. Then the photographic and diffractometer

data were combined, and two variable scale factors were introduced, one for each kind of data. After two more cycles of refinement, the  $R$  index was 0.096. At this point, seven of the eight hydrogen atoms were located unequivocally in a difference Fourier synthesis with peak heights ranging from 0.44 to 0.65 e.Å<sup>-3</sup> for the hydrogen atoms on the ring and from 0.40 to 0.44 e.Å<sup>-3</sup> for those on the methoxy group. One background peak height equaled 0.47 e.Å<sup>-3</sup> but the remainder of the background did not exceed 0.32 e.Å<sup>-3</sup>. Positive regions at potential positions for the eighth hydrogen ranging from 0.36 to 0.470 e.Å<sup>-3</sup> appeared near N(1), O(16) and O(13), corresponding to tautomers (I), (II), and (III) respectively. During six additional cycles of refinement the atomic coordinates of the seven hydrogen atoms were treated as variable parameters but they were arbitrarily assigned the anisotropic thermal factors of the atoms to which they were bonded. Although the  $R$  index was now at 0.064, all of the positive peaks at the various possible positions for the hydrogen atom in question persisted in the difference Fourier synthesis. These seemed plausible on the basis of the stereochemical details of the structural moieties that contained the H atom in question as the following data show: N(1)-H(1) 0.89, O(13)-H(13) 0.91, O(16)-H(16) 0.97 Å; C(2)-N(1)-H(1) 117, N(11)-O(13)-H(13) 119, C(5)-O(16)-H(16) 128°; H(1)···O(13) 1.99, H(1)···O(16) 2.05, H(13)···N(1) 1.88, H(13)···O(16) 2.28, H(16)···O(13) 2.10, H(16)···N(1) 2.68 and 2.99 Å, where the latter two distances are to N(1) atoms related by the  $c$ -glide; H(1)-N(1)···O(13) 38, H(1)-N(1)···O(16) 29, H(13)-O(13)···N(1) 30, H(13)-O(13)···O(16) 35, H(16)-O(16)···N(1) 74 and 68, and H(16)-O(16)···O(13) 23°.

Coordinates consistent with the structural formula (I) [*i.e.* N(1)-H] were then assigned on the basis of three observations. Firstly, the C(5)-O(16) and N(11)-O(13) bond lengths of 1.25 and 1.27 Å differ significantly from 1.35 and 1.33 Å which would be expected if protonation had occurred respectively at either O(16) or O(13). Secondly, the valency angle at N(1) is 123.8°, as compared with 116.2° in the unprotonated quinoline ring (Sax & Desiderato, 1967). Finally, 0.9 of the integrated electron count in the possible peaks for the hydrogen atom coincided with an N(1)-H bond even though the peak heights at the reasonable sites near N(1) and O(13) were both equal to 0.43 e.Å<sup>-3</sup> while the one near O(16) was 0.31 e.Å<sup>-3</sup>. The refinement was terminated after three cycles had been run with a modification of the Hughes scheme, where  $\sigma = C|F|$ , if  $|F| > 4F_{\min}$ , and  $\sigma = C4F_{\min}$ , if  $|F| \leq 4F_{\min}$ .  $4F_{\min}$  was set equal to 8 and  $C$  was a step function in  $\sin \theta$  that was derived from a plot of the range of  $\omega\Delta^2$  as a function of  $\sin \theta$ . It was assigned the values 0.153, 0.072, 0.111 and 0.125 in  $\sin \theta$  ranges 0.0-0.2, 0.2-0.8, 0.8-0.9, and 0.9-1.0 respectively. The  $R$  factor for 788 reflections of non-zero weight is 0.051 and for all of the 829 reflections it is 0.062. The corresponding weighted  $R$  factors are 0.066 and 0.070 respectively.

Table 1. Observed and calculated structure factors of 6-methoxy-8-nitro-5(1H)-quinolone

In each group of reflections with the same  $k$  and  $l$  indices, the columns are, from left to right, the  $h$  index,  $10|F_o|$ ,  $10|F_c|$ ,  $10A_c$  and  $10B_c$ . Following  $10|F_o|$ , a plus sign indicates that the intensity was collected photographically, while an asterisk denotes that the reflection was given zero weight in the least-squares refinement.

4	102	0	0	0	11	37	39	39-	0	12	61	63	38-	51	19	73	70	34	62	0	249	252	250-	33
6	220	244	244-	0	13	45	49	49-	0	14	229	251	14-	250-	20	12*	7	1	2	1	94	100	21	98
8	539	563	563	0	14	49	39	39-	0	14	33	34	4	34	21	41	43	4	43	2	53	58	54	19-
10	94	85	85	0	15	29	27	27	0	15	171	174	146-	96	21	48*	43	4	43	3	57	66	65	9
12	53	53	53	0	18	49*	42	42-	C	16	53	46	45	5	22	37*	37	17	33	4	37	30	30-	6
14	82	83	83-	0	17	98	98	98-	0	17	98	98	98-	6	23	32*	37	20	31-	5	25	28	12-	25-
16	25	19	19	0	0	616	597	597-	C	19	53	51	45	23	0	253	236	105-	211-	6	42*	45	25	35-
18	196	207	212-	0	1	73	100	100-	0	21	76	67	35	58-	0	196	195	178	78	8	31*	28	28-	4
22	97*	87	87	0	2	131	121	121-	0	4	1	1	1	4	1	1	1	1	1	7	55*	53	40-	53-
0	318	340	340-	0	3	98	100	100-	0	1	171	168	124-	114-	2	139	135	132	27-	9	24*	25	8	23
1	188*	246	246-	C	4	29	28	28	0	2	114	107	51-	94-	3	179	168	54	159	10	33*	31	24-	19
2	167	190	190	0	5	33	31	31	0	3	216	218	180-	123-	4	290	280	97-	263-	11	14*	19	17	8
3	179	177	177	0	6	82	81	81	0	4	122	115	7	115	5	473	466	449	123-	2	510	562	182	532
4	220	235	235	0	8	122	116	116-	0	5	110	105	104	16-	6	261	259	2	259	2	510	562	182	532
5	147	156	156	0	6	131	131	130	0	6	131	131	130	10-	7	94	92	88-	27	4	171	187	165	86
6	106	97	97-	0	9	45	41	41-	0	8	37	37	37	7-	8	122	122	45	113	6	122	127	117	48-
7	49	57	57-	0	10	33	36	36-	0	8	37	37	37	7-	9	118	115	36	109	8	69	70	37-	60
8	57	56	56-	0	14	36*	30	30	0	9	82	81	22-	78-	10	126	123	95	77-	10	159	169	45	163
9	196	201	201	0	15	45*	39	39	0	10	86	82	58-	58-	11	102	100	87-	49	12	86	83	66	50
10	298	283	283	0	0	53	63	63	0	11	65	65	65-	5-	12	204	219	61-	210-	14	65	63	57	26
12	82	78	78	0	1	73	81	81	0	12	98	97	94	27-	13	306	317	302	95-	16	69	66	56	34
13	29	30	30	0	2	12*	0	0	0	13	139	133	28	130-	14	220	220	153	158	18	69	74	40-	62
14	151	141	141	0	3	35	31	31	0	14	69	69	3-	69	15	57	57	27	47	20	53	54	17	53-
15	49	54	54	0	3	35	31	31	0	15	105	108	85	67	16	61	60	11	58	20	56*	54	14-	53-
16	57	57	57	0	4	49	46	46-	0	16	41	39	38-	7-	17	53	54	54-	0	0	56*	54	14-	53-
17	29	32	32-	0	5	16	6	6	0	17	69	66	66	1-	18	33	24	22	11	1	379	365	228-	285-
18	82	79	79	0	8	36*	37	37	0	18	53	48	23-	42-	19	57	53	10-	52-	2	204	193	26-	192
19	45	42	42	0	10	48*	43	43-	C	20	46*	39	32	21-	20	25	18	6-	17-	3	159	159	152-	47
21	29	21	21-	0	11	32*	32	32-	0	22	103	103	28	100-	22	20*	14	4	13-	4	220	218	153-	155-
0	481	489	489	0	0	99	88	88-	0	2	163	152	34-	148-	0	114	124	87	80	5	200	208	203	44
1	41	53	53-	0	3	122	122	122-	0	3	122	122	122-	83	0	114	124	87	80	6	126	124	99	77
2	69	71	71	0	4	65	59	59-	0	4	65	59	59-	5-	1	69	61	29	54-	7	135	131	130	14
4	286	302	302	0	5	37	39	32-	0	5	37	39	32-	23-	2	69	64	3	64	8	245	249	88-	233-
5	29	28	28-	0	6	73	70	68-	0	6	73	70	68-	17-	3	69	62	6-	62-	9	228	237	202-	123-
6	25	20	20-	0	7	82	77	73	24	4	73	76	76	4	4	73	76	76	4	10	143	133	108-	77
7	135	133	133-	0	8	559	593	599	584-	10	65	62	51-	34-	8	33	28	26-	11-	13	53	59	47-	37-
8	12*	13	13-	0	10	432	419	386-	161	11	82	80	44-	80-	9	33	30	8	29	14	114	110	103	37-
9	41	37	37-	0	12	98	95	93-	20-	12	53	56	38-	42-	11	131	124	50-	114-	15	102	99	88	31
10	90	88	88	0	14	151	150	62	137	13	77	80	62-	51-	12	53	60	58	14-	16	102	97	50-	83
11	57	56	56-	0	16	90	95	86-	39	14	41	34	21-	26-	13	163	156	110-	111	17	61	55	52	16
13	175	175	175-	0	18	102	106	106	7	17	44*	44	23-	38-	14	12*	10	10-	0	18	82	78	72	30
14	37	36	36	0	20	29	25	25	3	18	53*	47	46	11-	15	171	174	130	116-	19	37	29	11-	27
15	228	220	220	0	22	36*	25	25	21	1	102	103	28	100-	16	41	31	9	29-	20	29	30	7-	29
16	73	66	66-	0	22	171	156	130	87-	18	12*	16	16-	1	21	30*	29	26-	1	21	30*	29	26-	13-
18	25	9	9-	0	1	233	217	201	82	2	82	79	75-	27	19	33	36	36	4-	0	82	82	9-	83
19	33	28	28	0	2	579	616	282	548	4	61	62	62	4-	21	33*	29	29-	1-	1	82	84	9-	83
20	30*	6	6-	0	3	139	137	40-	131-	5	41	50	1	50	0	33	33	33	3	3	273	262	211	155-
21	40*	20	20-	0	4	335	350	344	69	6	57	57	40-	40-	0	33	33	33	3	3	339	330	302	134
22	84*	28	28-	0	5	281	289	124-	262-	7	33	33	15	29-	1	143	144	143	18-	4	339	330	302	134
0	45	70	70	0	6	175	174	139	106	8	131	131	36-	126	2	37	37	18	32-	5	90	95	78-	54
1	281	273	273	0	8	241	254	254	199	9	37	28	16-	23-	3	41	38	33	20-	6	175	182	22-	180
2	114	169	169	0	8	241	242	139-	199	10	110	117	97	66-	4	163	151	45	144	7	45	44	27	35-
3	65	67	67-	0	9	131	121	33-	109	11	33	21	15	15	5	265	257	254	42-	8	179	177	163	70
4	86	88	88-	0	10	241	239	207	118	12	25	20	18	10	6	118	111	29-	108-	9	69	71	60-	38
5	759	763	763	0	11	147	144	69-	127-	14	39*	41	21-	36-	7	102	102	49-	90	10	135	133	112	73-
6	69	68	68-	0	12	98	91	88	25	15	65	64	53-	36-	8	98	98	46-	87-	11	82	82	62	54-
7	90	88	88-	0	13	126	122	92-	80-	1	65	64	53-	36-	9	57	56	37	41	12	110	116	38-	109
8	37	30	30-	0	14	94	95	38	87	2	106	107	97-	46-	10	53	51	1	51	13	196	188	75-	172-
9	106	115	115-	0	15	53	49	44	22	3	49	49	49	1	11	98	95	89-	34	14	171	177	134	116
10	41	42	42	0	16	65	70	62	33	4	33	34	32-	12-	12	139	131	48	122	15	61	57	46-	34
11	175	169	169-	0	17	33	32	29	29	5	61	62	25	55	13	245	257	254	42-	16	45	44	33	20
12	12*	0	0	0	18	94	97	87-	42	6	25	20	8	19-	14	126	129	47-	120-	17	73	65	61-	23
13	547	577	577	C	19	37	29	29-	2	7	49*	47	47-	2	15	12*	2	2	1-	18	53	60	58-	14-
14	65	69	69	0	20	37	33	12-	31-	8	34*	37	28	25	16	29	31	21-	23-	19	41	39	38	7
15	37	30	30-	0	21	30*	5	4	3	10	64*	63	55-	30-	18	33*	26	24-	9	20	45*	31	30-	8-
17	82	81	81-	0	22	23*	28	24-	15	1	34*	33	27	20	20	43*	40	35	21	0	208	210	182-	104-
18	29	12	12-	0	1	400	394	298-	257-	2	51*	51	2	51-	0	416	385							

Table 1 (cont.)

19	36*	36	36	3	1C	41	44	34	28	6	32*	49	11-	48-	10	12*	5	5-	2-
						11	122	123	36-	117-	7	39*	26	26-	1-	65	70	48-	51
1	200	191	84-	172-	12	114	117	103	54-			0	L= 5		2	61	70	36-	11
2	139	140	118	75-	13	65	60	19-	57	2	114	120	120	13-	4	53	101	27-	97-
3	77	80	60-		14	98	97	91-	33-	4	228	230	1C1-	206-	4	53	65	53-	38-
4	82	78	43	64	15	82	78	42	66-	6	106	109	99	44	5	53	53	11-	52
5	98	100	86	51	16	61	59	39	43-	8	65	66	66-	0	6	33	25	25	1
7	86	91	71	56-	17	20	19	4	18-	12	53	52	52-	2-	7	12*	13	6	12
8	73	79	5	79	18	61	63	53-	34	14	143	139	74	118-	8	12*	4	1	4-
9	102	115	99-	59-	19	41*	56	49	28	16	90	91	10-	91	10	37	24	8-	29-
10	65	78	12	77-	21	26*	26	7-	25	18	61	64	13	35	11	40*	29	0	29-
11	41	38	9	37					20	41*	51	51-	49	12	16*	14	6	13-	4
12	61	66	63	17	0	94	98	78-	59-					13	57*	54	24-	49-	6
13	57	56	46-	32-	1	106	110	109	12	1	106	99	79-	59	14	58*	61	57-	23-
14	45	48	35-	33	2	45	45	37	25-	2	114	114	24	112					
15	31*	32	31	7-	3	57	54	54	3-	3	163	153	90	124-	4	53*	77	39	67
16	43*	39	15	36*	4	33	41	38	14-	4	200	198	186	69	6	45*	43	38-	22-
17	56*	54	51	18	5	65	59	58	13	5	90	84	25	80	7	52*	47	12	45-
					6	33	32	24	20	6	69	69	14-	67	8	24*	25	25	0
1	49	43	26-	34	7	86	89	29-	84	7	82	84	74-	40					
2	102	108	50-	96-	8	41	41	40-	9	8	53	58	51	26	2	36*	37	25	27-
3	57	70	26	65-	9	110	107	106	19	9	53	52	43-	28-					
4	37	36	24-	27-	10	33	31	31	3	10	12*	12	10-	5	0	147	149	9-	148-
6	29	28	20-	20	11	45	42	34-	24	11	90	86	83	23-	2	151	157	69	141-
7	29	21	9	19	12	12*	24	6-	23-	12	106	105	2-	104	4	155	147	126-	76-
8	25	16	2-	16-	13	61	59	59	4	13	102	106	33-	101-	6	208	209	154	141
9	12*	6	4-	10	2	14	122	122	115	41	8	57	57	53	22-	10	45	44	26
10	41	32	11-	30-	15	45	44	44	1-	15	69	63	35-	53	10	45	44	26	35-
11	42*	38	10	37-	16	12*	4	4	0	16	29	26	20	17-	12	224	231	206-	104-
12	36*	37	28-	23-	17	12*	17	2	17-	17	29	25	25-	3	14	188	198	195	37
13	30*	32	31-	8-	19	42*	60	1	60-	18	20*	28	27-	8	16	98	102	3	102
14	19*	21	16-	14-						19	37*	41	38	15-					
					C	314	297	238-	177	20	26*	26	22-	14-	0	61	63	49	40-
1	40*	33	32	10	1	286	272	198-	187-						1	45	45	20	40-
2	77*	60	19-	57-	2	126	121	21	119-	1	184	182	141-	116-	2	61	65	6	65
4	56*	48	27	39	3	118	114	57	99-	2	86	82	43-	70	3	37	38	6	38
4	39*	34	33	6	3	33	27	21	16-	3	53	53	2-	53	4	82	80	62	51-
6	33*	28	19-	21-	5	69	68	27	63-	5	41	36	20	30-	5	12*	8	8	2-
7	43*	39	8-	38-	6	98	99	98	12	6	118	121	102	66-	6	45	36	25-	26
8	53*	57	22	53	7	53	53	8-	52	7	114	119	118	7	8	12*	9	3	9-
9	43*	46	37	26	8	69	73	59-	44	8	102	94	47-	81-	9	12*	24	14	19-
					9	33	36	32-	16-	9	151	151	146-	35-	10	33	32	28	15
0	281	314	314	4-	10	41	47	34-	33-	10	82	78	120-	55-	11	73	65	60-	2
2	114	112	8	113	11	90	98	13-	97-	12	65	62	52-	53-	12	118	120	96	72-
4	188	191	170	89-	12	41	26	26-	5-	13	33	26	16	20-	13	61	61	52	32
6	65	70	39-	58-	13	41	32	6-	32	14	73	72	72	7-	14	90	97	87-	43-
10	73	73	72	13-	14	65	64	60	22	15	49	47	14	44	15	41	37	35-	14-
12	82	78	63	45-	15	94	95	56	77-	16	53	56	24-	51					
14	204	200	84-	182-	18	33*	43	24	36-	17	33	35	32	13	0	61	63	59	22
16	45	47	14	45						19	13*	14	14-	5	1	163	159	131	90-
18	29	19	8	17-	0	53	48	27-	40-	1	131	127	110	44-	2	94	97	25-	94-
					1	73	68	49	48	2	41	43	10-	113	3	34	30	10-	28
0	53	53	3*	41-	2	73	68	49	48	2	41	43	10-	42-	4	65	63	50	39-
1	277	254	245	65-	3	65	64	11-	63	3	94	95	56	76-	6	33	28	26	9
2	261	253	34	251-	4	73	79	17-	77	4	53	51	51	0	7	53	52	26-	46
3	171	160	6-	160	5	102	104	75	73-	5	49	48	46-	14-	8	33	35	35-	7-
4	208	198	78-	182-	6	61	61	40-	46-	6	37	30	17-	24	9	41	44	42	14
5	241	241	188	152-	7	41	47	41-	23	7	94	98	43	88-	10	53	48	48	2
6	192	194	69	181	8	29	37	10	36-	8	49	42	28-	31	12	20	17	8	15-
7	73	74	72-	19	9	57	70	9	69	9	73	75	C	75					
8	20	21	19	10	10	25	20	15-	14	11	65	64	45-	45-	0	37	34	21	26-
9	118	129	25-	127	11	69	81	56-	59	12	25	8	3-	8	1	367	363	322-	167-
10	102	96	89	37-	12	65	66	31	58	13	53	57	40-	41-	2	37	41	39	13-
11	86	89	59-	66	13	84*	149	119	50-	14	12*	9	9	1	3	11C	111	39	104-
12	159	160	101-	124	14	54*	80	55-	58-	15	45	51	27	43-	5	73	71	25	67-
13	224	228	176	145-	16	35*	44	24-	37-	17	69	69	45-	52-	6	45	43	38	20
14	184	176	158	76											7	98	104	71	75
15	53	54	6	54	C	94	84	84-	8-	1	184	188	129-	137-	8	12*	5	2-	5
16	102	103	18	101	1	49	44	21-	38-	2	143	138	123	61-	9	29	31	31-	5-
17	12*	11	11-	0	2	45	46	15-	44-	3	41	41	41	2	11	73	85	7-	85-
19	53	47	44-	18-	3	33	46	46	4	4	29	26	19	18-	12	33	28	15	24-
					4	33	48	26-	40	5	33	30	29-	6-	13	25	25	2	24-
0	653	633	493	397-	5	41	47	36-	30-	6	98	99	95-	26	0				
1	453	431	228-	365-	8	16	15	11-	10-	7	57	59	52	27-	0	114	113	108-	4
2	216	216	89	197	9	25	25	3	8	73	80	37	71	1	102	102	57-	5	33
3	122	123	25-	120-	10	24*	29	28-	5	9	106	111	105-	21-	2	73	75	73	17
4	61	63	24	58						10	57	63	12	61-	3	53	53	13	51
5	41	34	23	25-	1	25*	38	38-	3-	12	33	37	18	33	4	41	42	33-	26
6	102	100	80-	61	2	53*	76	24-	72	14	36*	32	25-	19	6	25	19	14	13
7	73	69	24	65	3	36*	36	1-	36-	15	38*	37	29-	22	7	41	39	39-	8
8	98	101	62	79-	4	33*	33	32	9	16	32*	21	13	16-	8	20	24	10	22-
9	73	68	22-	65-	5	44*	50	44-	24	17	37*	45	41	17	9	45	51	43	27

The standard deviation of an observation of unit weight  $\{\sum w[F_o - KF_c]^2/(NO - NP)\}^{\frac{1}{2}}$ , where  $NO$  is the number of observations and  $NP$  is the number of varied parameters, is 0.776. The observed and calculated structure factors appear in Table 1. The atomic coordinates, their thermal parameters and the estimated standard deviations are given in Tables 2 and 3. The key to atomic numbering is given in Fig. 1. The atomic form factors used in the refinement are taken from *International Tables for X-ray Crystallography* (1962).

## Discussion

### The molecular and crystal structure

Since positive peaks, estimated to be 1-2  $\sigma$  in the electron density, appear in the final difference synthesis

at positions near O(13) and O(16) consistent with (II) and (III) respectively, it is uncertain whether the molecule exists in tautomeric forms or in a single configuration of the atoms. The results in Table 4 would be regarded as weighted averages of parameters in the tautomers, whereas in a single configuration of atoms they could be analyzed in terms of resonance structures. In either case, the cross conjugated structure (I) makes the largest contribution to the observed molecular parameters, although the aromatic (II) and acinitro (III) structures are significant too, as is evident from the bond lengths in the keto and nitro groups. The C(8)-N(11) bond is considerably shorter than commonly observed in nitro groups (Williams, 1967) and the orientation of this group is favorable for  $\pi$  bonding between C(8) and N(11) as it deviates by only 7.0° from copla-

Table 2. Fractional atomic coordinates and their estimated standard deviations

	Fractional coordinates $\times 10^4$		
	x	y	z
N(1)	2546 (2)	5678 (5)	2429
C(2)	3247 (2)	5588 (7)	2336 (10)
C(3)	3593 (3)	3914 (7)	1606 (10)
C(4)	3174 (2)	2337 (7)	868 (10)
C(5)	1995 (2)	705 (6)	197 (9)
C(6)	1233 (3)	957 (6)	316 (9)
C(7)	935 (2)	2664 (6)	1089 (9)
C(8)	1345 (2)	4284 (6)	1846 (8)
C(9)	2099 (2)	4184 (5)	1751 (8)
C(10)	2426 (2)	2431 (5)	938 (9)
N(11)	976 (2)	5880 (5)	2726 (8)
O(12)	317 (2)	5757 (5)	2901 (8)
O(13)	1324 (1)	7376 (4)	3347 (8)
O(14)	866 (2)	-662 (5)	-434 (8)
C(15)	105 (3)	-688 (9)	-197 (10)
O(16)	2297 (2)	-797 (4)	-482 (9)

	Fractional coordinates $\times 10^3$		
	x	y	z
H(1)	236 (3)	671 (8)	305 (10)
H(2)	345 (3)	704 (10)	288 (9)
H(3)	412 (4)	382 (10)	152 (10)
H(4)	340 (3)	127 (11)	46 (10)
H(7)	44 (3)	276 (9)	104 (11)
H(8)	-17 (4)	44 (12)	-85 (11)
H(9)	-6 (3)	-210 (11)	-79 (11)
H(10)	-5 (4)	-69 (10)	112 (11)

narity with the ring. This conformation and the negative charge on the nitro oxygen atoms is stabilized further by the internal hydrogen bond between N(1) and O(13). In 5-acetoxy-6-methoxy-8-nitroquinoline, on the other hand, the aromatic form contributes 91 percent to the resonance structure while the cross conjugated and quinoidal forms are negligible contributors, so that there is little  $\pi$  bonding between the ring and any of the substituents.

The shape and conformation of the molecule and the molecular packing are shown in Figs. 1 and 2. The ten atoms of the fused ring are within 0.015 Å of the least-squares plane, 0.01202X-0.48307Y-0.87549Z = -0.05052, where the coordinates are ex-

pressed in Å units and are referred to the crystallographic axes. However, the probability that the small displacements from the ring are non-random is  $\geq 0.99$  since the  $\chi^2$  value is 20. The respective displacements of atoms N(11), O(12), O(13), O(14), C(15) and O(16) from the plane are 0.059, 0.266, 0.028, -0.088, 0.081 and -0.030 Å. The method of Scho-

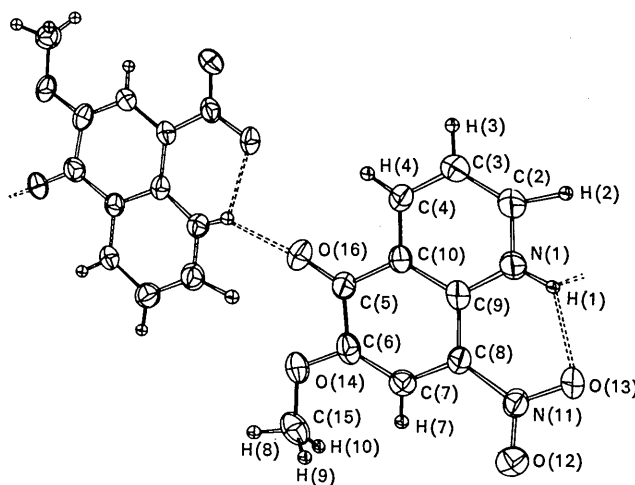


Fig. 1. Inter- and intramolecular hydrogen bonding shown in two molecules of a hydrogen bonded chain in crystalline 6-methoxy-8-nitro-5(1H)-quinolone.

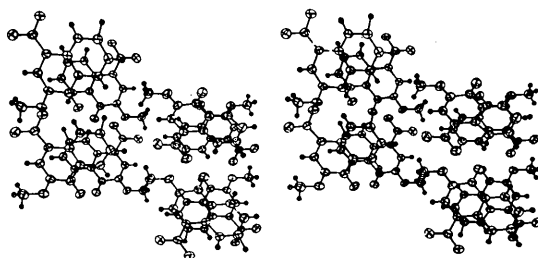
Fig. 2. A stereoscopic view along *c* showing the molecular packing in 6-methoxy-8-nitro-5(1H)-quinolone.

Table 3. Anisotropic thermal parameters and their e.s.d. in the form:

	$\exp[-(h^2\beta_{11} + \dots + 2kl\beta_{23})]$					
	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
N(1)	219 (10)	151 (7)	129 (8)	-1 (3)	-3 (3)	-19 (7)
C(2)	247 (13)	181 (11)	152 (9)	-3 (3)	5 (3)	-22 (9)
C(3)	228 (13)	226 (13)	186 (10)	-8 (4)	3 (3)	-32 (10)
C(4)	238 (13)	166 (11)	152 (10)	10 (3)	-1 (3)	-16 (8)
C(5)	251 (14)	171 (11)	137 (10)	6 (3)	-4 (3)	-15 (10)
C(6)	272 (14)	152 (10)	131 (9)	-8 (3)	-5 (3)	-27 (9)
C(7)	217 (12)	168 (11)	144 (8)	6 (3)	-1 (3)	-3 (8)
C(8)	218 (12)	136 (10)	140 (11)	7 (3)	-2 (3)	-24 (8)
C(9)	246 (12)	121 (9)	88 (8)	-1 (3)	-4 (3)	6 (7)
C(10)	232 (12)	152 (8)	113 (8)	0 (3)	0 (3)	11 (7)
N(11)	230 (11)	134 (8)	139 (8)	10 (2)	6 (3)	-17 (7)
O(12)	226 (9)	220 (9)	228 (9)	12 (2)	4 (2)	-5 (7)
O(13)	269 (9)	157 (7)	215 (8)	-1 (2)	3 (2)	-74 (7)
O(14)	294 (10)	176 (8)	201 (8)	-15 (3)	-2 (3)	-73 (7)
C(15)	262 (16)	253 (15)	177 (12)	-14 (4)	-14 (4)	-12 (11)
O(16)	307 (13)	199 (8)	246 (10)	15 (2)	10 (3)	-95 (8)

Table 4. Bond lengths and angles

The e.s.d.'s in parentheses refer to the last digit. Where two values appear for a bond length, the effect of the thermal motion has been excluded in the first figure while the second includes a correction based upon the assumption of a 'riding' motion for the atoms (Busing & Levy, 1964).

<i>i</i>	<i>j</i>	<i>k</i>	Angle ( <i>ijk</i> )	Distance ( <i>ij</i> )
C(9)	N(1)	C(2)	123.8 (4)°	1.368 (5) Å
H(1)	N(1)	C(2)	117 (4)	0.89 (6)
H(1)	N(1)	C(9)	119 (4)	
N(1)	C(2)	C(3)	121.8 (5)	1.311 (6)
N(1)	C(2)	H(2)	106 (4)	
H(2)	C(2)	C(3)	132 (4)	1.08 (6)
C(2)	C(3)	C(4)	117.8 (6)	1.367 (8)
C(2)	C(3)	H(3)	123 (4)	
H(3)	C(3)	C(4)	119 (4)	0.99 (7)
C(3)	C(4)	C(10)	120.8 (5)	1.393 (8)
C(3)	C(4)	H(4)	116 (5)	
H(4)	C(4)	C(10)	123 (5)	0.86 (8)
C(4)	C(10)	C(5)	119.7 (5)	1.398 (6)
C(4)	C(10)	C(9)	118.6 (5)	
C(5)	C(10)	C(9)	121.6 (5)	1.477 (6)
C(10)	C(5)	O(16)	119.7 (5)	
C(10)	C(5)	C(6)	115.5 (5)	
O(16)	C(5)	C(6)	124.8 (5)	1.227 (6); 1.250
C(5)	C(6)	O(14)	112.6 (5)	1.433 (6)
C(5)	C(6)	C(7)	121.5 (5)	
O(14)	C(6)	C(7)	125.8 (5)	1.366 (6); 1.377
C(6)	C(7)	C(8)	123.0 (5)	1.359 (7)
C(6)	C(7)	H(7)	116 (4)	
H(7)	C(7)	C(8)	121 (4)	0.93 (7)
C(7)	C(8)	C(9)	119.1 (5)	1.411 (7)
C(7)	C(8)	N(11)	117.6 (5)	
N(11)	C(8)	C(9)	123.3 (5)	1.403 (6); 1.404
C(8)	C(9)	C(10)	119.2 (4)	1.408 (6)
C(8)	C(9)	N(1)	123.8 (4)	
C(10)	C(9)	N(1)	117.0 (4)	1.418 (6)
C(8)	N(11)	O(12)	119.7 (5)	
O(13)	N(11)	C(8)	118.8 (4)	1.249 (5); 1.265
O(12)	N(11)	O(13)	121.4 (5)	1.238 (5); 1.255
C(6)	O(14)	C(15)	116.8 (5)	
O(14)	C(15)	H(8)	115 (4)	1.432 (6); 1.434
O(14)	C(15)	H(9)	104 (4)	
H(10)	C(15)	O(14)	113 (4)	1.06 (7)
H(8)	C(15)	H(9)	104 (6)	1.01 (8)
H(9)	C(15)	H(10)	110 (6)	1.06 (7)

maker, Waser, Marsh & Bergman (1959) was used for the least-squares plane calculation. The plane of the fused ring system intersects the *ab* plane in a 28.9° angle, and fused rings in molecules related by the *c*-glide lie in planes that deviate 1.4° from parallel. The intermolecular contacts between *c*-glide related molecules are the normal van der Waals variety. In the bifurcated hydrogen bond shown in Fig. 1, H(1) is shared by an intramolecular hydrogen bond between N(1) and O(13) and by a strong intermolecular hydrogen bond linking N(1) to O(16) in a molecule related by the *c*-glide and a unit translation  $-b$ . With the exception of two somewhat close intermolecular contacts involving H(2), which are listed in Table 5 together with the hydrogen bond parameters, the non-bonded contacts were the normally expected ones.

#### The dielectric constant

The two maxima at positions for the hydrogen atoms in (II) and (III) were 0.14 and 0.12 e.Å<sup>-3</sup> respectively

Table 5. Some intermolecular distances and angles

Atoms*	Distance	Angle
N(1)···O(16)	2.779 (5) Å	
N(1)···O(13)	2.620 (5)	
O(13)···O(16)	2.963 (5)	
H(1)···O(16)	2.05 (6)	
H(1)···O(13)	1.99 (6)	
N(1)-H(1)···O(16)		139 (6)°
N(1)-H(1)···O(13)		126 (5)
H(2)···O(14)	2.34 (7)	
C(2)···O(14)	3.377 (7)	
H(2)···O(16)	2.33 (7)	
C(2)···O(16)	3.028 (5)	
H(2)-C(2)···O(14)		14 (3)
H(2)-C(2)···O(16)		41 (4)

\* H(1), N(1) and O(13) are in the same molecule but O(14) and O(16) are in the molecule related by the *c*-glide and the translation (0, *b*, 0).

in the final difference map compared with an average background peak of 0.12 e.Å<sup>-3</sup>, so that they are possibly errors in the electron density. On the other hand, Cady & Larson (1965) interpreted similar peaks in the difference map of 1,3,5-triamine-2,4,5-trinitrotoluene as N-H bonding electrons delocalized in the H...O region of the N-H...O hydrogen bond. They repre-

(-)  
sented the bonding by resonance structures N-H O

(-)  
and N H-O. The same explanation could apply here *i.e.* that these two residual peaks are N-H bonding electrons delocalized in the region near O(16) and O(13). Since the crystal structure analysis of (I) indicated an orientation of the polar hydrogen atom, which is attached to nitrogen, facing the keto-oxygen and one of the strongly polar oxygens of the nitro group (Fig. 1), it was conjectured whether this hydrogen might be labile enough to be transferred by an electric field to an adjacent oxygen atom. This would be expected to result in a high polarizability and dielectric constant, and if the proton were transferred intermolecularly an abnormally high dielectric loss should also occur since the crystal would be rendered conductive by the proton transfer. The dielectric constant and loss tangent of this compound were determined over a range of frequencies from 60 Hz to 10<sup>10</sup> Hz to find evidence for the proton transfer polarization, if it occurs.

The dielectric measurements on the crystalline powder were made by compacting the powder into a measurable volume in some tests, and in others by vacuum impregnating the powder with a pure paraffin wax. Measurements on these specimens were made over a wide frequency range, up to 10<sup>5</sup> Hz with a General Radio 716 bridge and from 10<sup>6</sup> Hz to 5 × 10<sup>7</sup> Hz with the susceptance variation method resonant circuit technique. Several measurements were made with a resonant cavity at 2 × 10<sup>8</sup> Hz. A single measurement was made at 9.5 × 10<sup>9</sup> Hz in a shorted wave guide. In this latter case, a paraffin impregnated powder was formed into a rectangular parallelepiped. The apparent density of the dry powder specimens varied, depending on the

compression, between 0.77 and 0.95. From these values and the crystal density, 1.595, the volume fraction of the powder during measurement could be computed, and it ranged in different tests between 0.48 and 0.59.

The experimentally obtained dielectric constants were, of course, lower than that of the crystal because part of the volume measured was air or paraffin. The formula developed by Böttcher (1945) and confirmed by van Vessem & Bijvoet (1948) gave consistent and reasonable values of the solid crystal dielectric constant. These values ranged from 2.24 to 3.19 for the specimen and yielded calculated values for the crystal of 4.37 to 4.47, with one value out of this range at 4.05. These values were calculated from three different apparent density specimens, and one wax-filled specimen. The Böttcher equation (rearranged) is:

$$K_1 = \frac{2(K - K_2) + 2K_2\delta}{3K\delta - (K - K_2)} K,$$

where  $K_1$  is the dielectric constant of the solid,  $K_2$  of the suspending medium and  $K$  of the mixture, and  $\delta$  is the volume fraction of solid.

The dielectric constant values for these crystals are at a level which is typical of compounds of a similar nature, where no proton transfer is suspected. For example, the dielectric constant of 2-methoxy-4-nitroaniline is 3.91 and of 2-methoxy-5-nitroaniline is 4.01, as reported by Rao (1965). The very small dispersion (decline) in dielectric constant between 60 and  $10^{10}$  Hz indicates that no proton transfer or other very significant polarization process is limited within this frequency range. Very likely the polarization in the crystal is of an atomic (intramolecular polar vibration or rotation) process whose absorption and dispersion region lies in the infrared frequency range.

The resistivity of this material was shown to be very high and the loss tangent ( $\tan \delta$ ) was found to be quite low (0.0006 to 0.0018) over most of the frequency range. There was some evidence of a small (specimen  $\tan \delta_{\max} < 0.006$ ) dispersion region in the vicinity  $10^7$

to  $10^8$  Hz but this was not delineated exactly. This low conductivity and low loss was consistent with the nearly constant level of dielectric constant over the wide frequency range studied. It certainly precluded any very significant continuous or discontinuous charge transfer through these crystals.

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### References

- BÖTTCHER, C. J. F. (1945). *Rec. Trav. chim. Pays-Bas*, **64**, 47.  
 BUERGER, M. (1959). *Vector Space*, p. 252. New York: John Wiley.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS, A FORTRAN Crystallographic Least-Squares Program. Oak Ridge National Laboratory, Tennessee.  
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.  
 CADY, H. H. & LARSON, A. C. (1965). *Acta Cryst.* **18**, 485.  
 CORFIELD, P. W. R. (1965). *Solution of the Patterson Function by Superposition Methods*, Technical Report. The Crystallography Laboratory, University of Pittsburgh.  
 CORFIELD, P. W. R. & ROSENSTEIN, R. D. (1966). *Trans. Amer. Cryst. Ass.* **2**, 17.  
 ELDERFIELD, R. C., GENSLER, W. J., WILLIAMSON, T. A., GRIFFING, J. M., KUPCHAN, S. M., MAYNARD, J. T., KREYSA, F. J. & WRIGHT, J. B. (1946). *J. Amer. Chem. Soc.* **68**, 1584.  
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **65**, 1737.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.  
 RAO, S. R. (1965). *Current Sci.* **34**, 455.  
 SAX, M. & DESIDERATO, R. (1967). *Acta Cryst.* **23**, 319.  
 SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.  
 VESSEM, J. C. VAN & BIJVOET, J. M. (1948). *Rec. Trav. chim. Pays-Bas*, **67**, 191.  
 WILLIAMS, D. E. (1967). Private communication.