A NITRO GROUP DISTORTING 2-QUINOLONE SKELETON

Nagatoshi Nishiwaki, Chitose Tanaka, Motoki Asahara, Noriko Asaka,†
Yasuo Tohda,†† and Masahiro Ariga*

Department of Chemistry, Osaka Kyoiku University,
† Center for Instrumental Analysis, Osaka Kyoiku University,
†† Division of Natural Science, Osaka Kyoiku University,
Asahigaoka 4-698-1, Kashiwara, Osaka 582-8582, Japan

Abstract - 1-Methyl-3,6,8-trinitro-2-quinolone shows high reactivity compared with 1-methyl-3,6-dinitro-2-quinolone. It was found the 8-nitro group activates a 2-quinolone ring sterically rather than electronically.

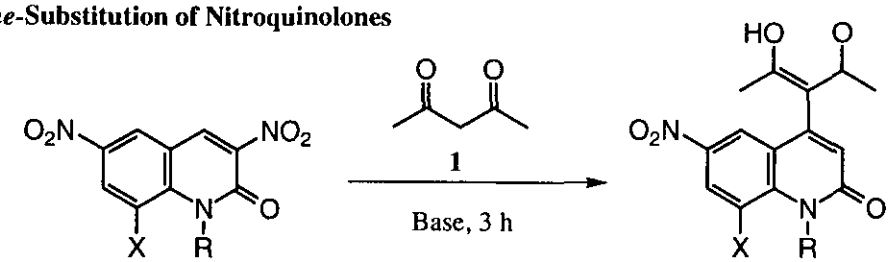
There are more than two hundred reports dealing a wide range of quinoline alkaloids from the Rutaceae family.[1] The majority of them has a 1-methyl-2-quinolone skeleton.[2] From the viewpoint of biochemical activity, it is important to introduce various functional groups into a quinolone ring. In the mainly used methods for functionalization, the pre-introduced substituent such as OH, OR, =O and NR_2 groups is built into the skeletons.[3]

In our previous paper,[4] we indicated the *cine*-substitution of 1-methyl-3,6,8-trinitro-2-quinolone (TNQ-Me) effectively caused regioselective C-C bond formation and enabled functionalization at the 4-position directly. The starting quinolone has three nitro groups, but it has not been sure whether two of them on the benzene ring are necessary or not for this reaction. In the present work, we studied the effect of the nitro group far from the reaction site on the reactivity of the 4-position using 1-methyl-3,6-dinitro-2-quinolone (DNQ-Me). We show that the 8-NO_2 group affects on a 2-quinolone ring sterically rather than electronically.

The *cine*-substitution with 2,4-pentanedione (**1**) under basic conditions was employed for comparing reactivities of nitroquinolones. The reaction of TNQ-Me with **1** in EtOH in the presence of NEt_3 readily proceeded to afford *cine*-substituted product (**2**) in 88 % yield. On the other hand, DNQ-Me and DNQ-Et were entirely recovered under the same conditions or even at reflux temperature. Trace amount of product (**3**) was detected when EtONa was employed as the base. The yield of **3** could be improved by using DMF as the solvent instead of EtOH.

The 8-NO_2 group obviously activates a 2-quinolone ring in a great way, however, the NO_2 group is far from the reaction site. In cooperation with the fact that demethylated trinitroquinolone[5] TNQ-H was recovered intact on treatment with **1** in the presence of NEt_3, we suppose that the activation of TNQ-Me results from steric repulsion between 8-NO_2 and 1-Me groups.

Table 1 ***cine*-Substitution of Nitroquinolones**

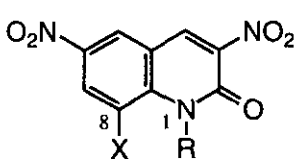


2-4

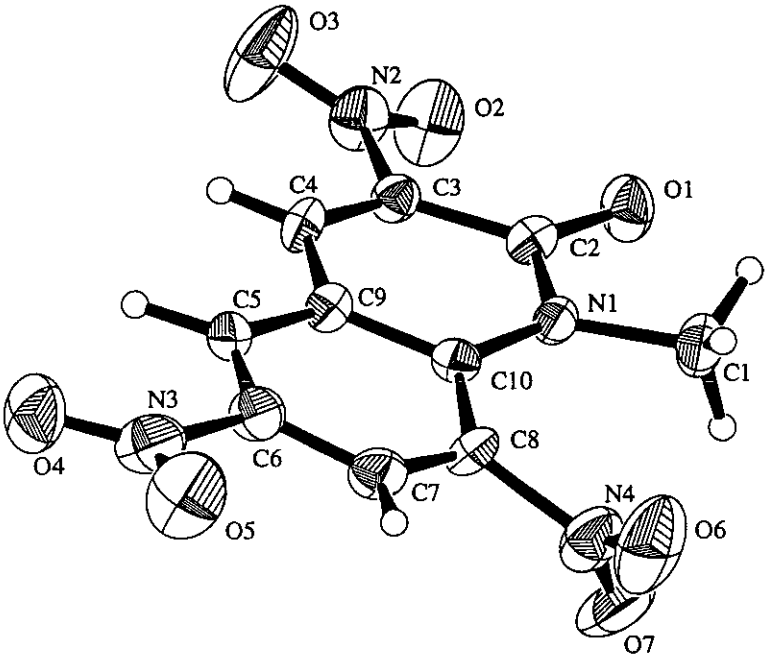
Substrate			Solv.	Base	Temp. / °C	Product	Yield / %
X	R						
NO_2	Me	(TNQ-Me)	EtOH	NEt_3	rt	**2**	88
H	Me	(DNQ-Me)	"	"	"	**3**	0
H	Et	(DNQ-Et)	"	"	"	**4**	0
H	Me	(DNQ-Me)	"	"	reflux	**3**	0
			"	EtONa	rt		trace
			DMF	NEt_3	50		35
			"	EtONa	rt		62
NO_2	H	(TNQ-H)	EtOH	NEt_3	rt	**4**	0

MOPAC (PM3) molecular orbital calculations for TNQ-Me, DNQ-Me and TNQ-H were conducted by using CAChe system. In the case of TNQ-Me, the 8-NO_2 group has no coplanarity with the quinoline ring, which turns through 67.7°. Furthermore the 2-quinolone ring is torsionally strained by the steric compression of substituents at the peri-positions. The dihedral angle between C8-NO_2 bond and N1-Me one is 30.0°. On the other hand, similar strains are not observed in cases of desubstituted quinolones, DNQ-Me and TNQ-H.

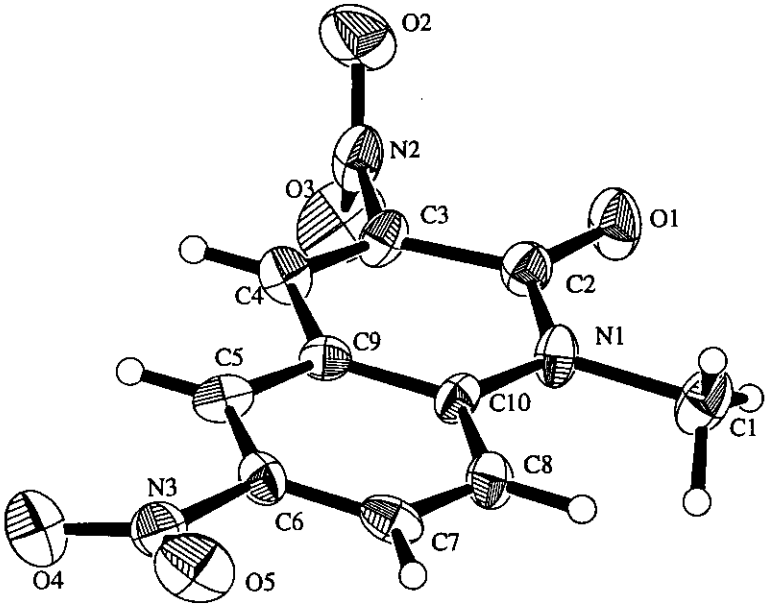
Table 2 Dihedral angles between N1-R and C8-X bonds



X	R		Dihedral Angle	
			Estimated	Actual
NO_2	Me	(TNQ-Me)	30.0 °	25.0 °
H	Me	(DNQ-Me)	0.67 °	0.9 °
NO_2	H	(TNQ-H)	0.04 °	—



An ORTEP (30 % probability ellipsoids) view of TNQ-Me



An ORTEP (30 % probability ellipsoids) view of DNQ-Me

Above calculated results were supported by X-Ray analyses. The 8-NO_2 group of TNQ-Me turned through 55.8°, and the quinolone ring was confirmed to be considerably strained compared with DNQ-Me. It was also turned out that two independent molecules in the crystal of DNQ-Me have almost same structure except for several torsion angles as shown in Table 4. In the NMR spectra, apparent electronic effect of the 8-NO_2 group on the pyridone ring was not observed.

We suggest a plausible reason for remarkable activity of TNQ-Me as follows. Steric repulsion between 8-NO_2 and 1-Me groups distorts the quinolone skeleton, in which the pyridone ring cannot be coplanar with the benzene ring. As a result of the distortion, the aromaticity of the pyridone moiety decreases although it is originally low. Thus, the pyridone ring reveals nitroalkene property rather than aromatic one,[6] and high reactivity is attained at the 4-position.

It was considered that 3,6-dinitro-2-quinolone bearing a bulky group at the 1-position was sterically activated similarly, but the Et group was not bulky enough to distort 2-quinolone skeleton.

Although further investigation is still necessary, the present work provides a fundamental information about chemical behavior of 1-substituted 2-quinolone derivatives. By using this steric repulsion between substituents, functionalization of 2-quinolones or activation of other inert condensed systems may be possible.

EXPERIMENTAL

All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental microanalyses were performed using a Yanaco MT-3 CHN corder. IR spectra were recorded on a Horiba FT-200 infrared spectrophotometer. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR (100 MHz) were obtained on a Bruker DPX-400, and chemical shifts are reported in ppm on the δ scale from internal TMS. All reagents and solvents were commercially available and used as received.

1-Substituted 2-quinolones

Two well-known preparative methods for 1-substituted 2-quinolones were employed.

a) Alkylation of Quinoline-Oxidation: Following the procedure described for 1-methyl-2-pyridone,[7] quinoline was alkylated and oxidized using three times amount of solvent which was used in the literature.

b) Oxidation-Alkylation: 2-Quinolone was prepared from quinoline *N*-oxide,[8] and was treated with alkyl halide in the presence of KOH.

Nitration of 2-Quinolones[5]

Nitration of 1-methyl-2-quinolone with fuming HNO_3 (d = 1.52) gave TNQ-Me in 90 % yield.[4] When 15 *M* HNO_3 and 18 *M* H_2SO_4 were used, DNQ-Me was mainly obtained.

TNQ-Me:[4] ^{1}H NMR (DMSO-d_6) δ = 3.48 (s, 3H), 9.07 (d, *J* = 2.6 Hz, 1H), 9.24 (d, *J* = 2.6 Hz, 1H), 9.32 (1H, s); ^{13}C NMR (DMSO-d_6) 154.4 (s, C-2), 140.8, 140.8, 138.4, 137.6 (s, C-4a, C-6, C-8, C-8a), 136.4 (d, C-4), 130.4 (d, C-7), 124.8 (d, C-5), 120.1 (s, C-3), 35.2 (q, *N*-Me).

1-Methyl-3,6-dinitro-2-quinolone (DNQ-Me)

To cold 18 *M* H_2SO_4 (8.5 mL), 1-methyl-2-quinolone (1.6 g, 10 mmol) was gradually added. After gradual addition of 15 *M* HNO_3 (16.0 mL), the mixture was heated at 80 °C for 5 h. The solution was cooled down to rt, and H_2O (100 mL) was poured into the reaction mixture. The generated yellow

precipitates (2.4 g) were collected. ^{1}H NMR (DMSO-d_6) showed this product was a mixture of four nitrated 2-quinolones (DNQ-Me: 41 %, 6,8-dinitro derivative: 30 %, TNQ-Me: 9 %, 6-nitro derivative: 19 %). Each signals were assigned as follows. 1-Methyl-6,8-dinitro-2-quinolone:[5] δ = 3.34 (s, 3H), 6.95 (d, J = 9.6 Hz, 1H), 8.28 (d, J = 9.6 Hz, 1H), 8.87 (d, J = 2.2 Hz, 1H), 9.02 (d, J = 2.2 Hz, 1H): 1-Methyl-6-nitro-2-quinolone:[5] δ = 3.65 (s, 3H), 6.75 (d, J = 9.6 Hz, 1H), 7.68 (d, J = 9.3 Hz, 1H), 8.09 (d, J = 9.6 Hz, 1H), 8.53 (dd, J = 9.3, 2.3 Hz, 1H), 8.68 (d, J = 2.3 Hz, 1H). Recrystallization of the mixture from PhH and successively from EtOH afforded DNQ-Me as yellow needles (0.52 g, 21 %). DNQ-Me: mp 256-258 °C; IR (Nujol) 1670, 1599, 1524, 1342 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 3.74 (s, 3H), 7.83 (d, J = 9.5 Hz, 1H), 8.53 (dd, J = 9.5, 2.0 Hz, 1H), 8.93 (d, J = 9.5 Hz, 1H), 9.09 (1H, s); ^{13}C NMR (DMSO-d_6) 154.6 (s, C-2), 145.2, 143.2, 141.9 (s, C-4a, C-6, C-8a), 137.0 (d, C-4), 128.7, 128.0 (d, C-5, C-7), 117.9 (d, C-8), 117.4 (s, C-3), 31.7 (q, *N*-Me). Anal. Calcd for $C_{10}H_7N_3O_5$: C, 48.20; H, 2.83; N, 16.86. Found: C, 48.05; H, 2.89; N, 16.70.

Crystal data for TNQ-Me

$C_{10}H_6N_4O_7 \bullet C_6H_6$, M = 372.29, orthorhombic, space group $P2_12_12_1$, a = 12.403 (3) Å, b = 9.150 (4) Å, c = 7.175 (1) Å, V = 1704.2 (5) Å^3, D_c = 1.451 g/cm^3, Z = 4, F(000) = 768.00, μ = 1.17 cm^{-1}. A yellow crystal of dimensions 0.30 x 0.30 x 0.40 mm was sealed in a glass capillary and used for measurement at 293 K on a Rigaku AFC7R four-circle diffractometer employing graphite monochromated MoKα radiation (λ = 0.71069 Å) using the ω/2θ scan technique. The 2279 unique reflections were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRILL88). The final full-matrix least squares refinement, based on F using 892 reflections (I > 3.00σ (I)) and 292 parameters, converged with R = 0.039 and R_w = 0.028.

Crystal data for DNQ-Me

$C_{10}H_7N_3O_5$, M = 249.18, orthorhombic, space group $P2_12_12_1$, a = 13.892 (6) Å, b = 14.97 (1) Å, c = 10.010 (9) Å, V = 2081 (2) Å^3, D_c = 1.590 g/cm^3, Z = 8, F(000) = 512.00, μ = 1.31 cm^{-1}. A yellow crystal of dimensions 0.30 x 0.30 x 0.40 mm was used for measurement at 293 K on a Rigaku AFC7R four-circle diffractometer employing graphite monochromated MoKα radiation (λ = 0.71069 Å) using the ω/2θ scan technique. The 2727 unique reflections were corrected for Lorentz and polarization effects. The structure was solved by direct methods (MITHRILL88). The final full-matrix least squares refinement, based on F using 1088 reflections (I > 3.00σ (I)) and 325 parameters, converged with R = 0.049 and R_w = 0.040.

***cine*-Substitution of DNQ-Me**

The sodium enolate was prepared from 2,4-pentanedione (**1**, 122 μL, 1.2 mmol) and 0.2 *M* NaOEt in EtOH (7.5 mL, 1.5 mmol). After removal of EtOH, the resultant enolate was dissolved in DMF (20 mL). To this solution, a solution of DNQ-Me (249 mg, 1.0 mmol) in DMF (20 mL) was added at rt over 30 min, and the solution color became brown. After being stirred for a further 3 h, the mixture was quenched with 1 *M* HCl (1.4 mL). DMF was removed under reduced pressure, and the residue was dissolved into $CHCl_3$ (50 mL). The organic layer was washed with H_2O (60 mL x 3), dried over ($MgSO_4$) and concentrated. The residue was column chromatographed on silica gel to give *cine*-substituted product (**3**, 168 mg, 53 %) which was eluted with hexane-$CHCl_3$ (1/1).

Table 3 Bond Angles and Distances for TNQ-Me

Bond Angles Involving the Nonhydrogen Atoms[a]

atom	atom	atom	angle
C(1)	N(1)	C(2)	113.8(6)
C(1)	N(1)	C(10)	122.3(6)
C(2)	N(1)	C(10)	123.6(5)
O(2)	N(2)	O(3)	123.3(6)
O(2)	N(2)	C(3)	118.4(6)
O(3)	N(2)	C(3)	118.3(6)
O(4)	N(3)	O(5)	125.6(7)
O(4)	N(3)	C(6)	117.6(7)
O(5)	N(3)	C(6)	116.8(7)
O(6)	N(4)	O(7)	126.5(7)
O(6)	N(4)	C(8)	118.0(8)
O(7)	N(4)	C(8)	115.4(8)
O(1)	C(2)	N(1)	119.3(6)
O(1)	C(2)	C(3)	126.9(6)
N(1)	C(2)	C(3)	113.7(6)
N(2)	C(3)	C(2)	118.7(6)
N(2)	C(3)	C(4)	117.8(6)
C(2)	C(3)	C(4)	123.4(6)
C(3)	C(4)	C(9)	121.5(6)
C(6)	C(5)	C(9)	119.7(6)
N(3)	C(6)	C(5)	119.9(6)
N(3)	C(6)	C(7)	118.8(6)
C(5)	C(6)	C(7)	121.2(6)
C(6)	C(7)	C(8)	119.6(6)
N(4)	C(8)	C(7)	115.0(6)
N(4)	C(8)	C(10)	122.3(6)
C(7)	C(8)	C(10)	122.4(6)
C(4)	C(9)	C(5)	121.2(6)
C(4)	C(9)	C(10)	117.4(6)
C(5)	C(9)	C(10)	121.4(6)
N(1)	C(10)	C(8)	125.0(5)
N(1)	C(10)	C(9)	119.8(6)
C(8)	C(10)	C(9)	115.2(5)

a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Bond Distances Involving the Nonhydrogen Atoms[b]

atom	atom	distance
O(1)	C(2)	1.209(7)
O(2)	N(2)	1.221(7)
O(3)	N(2)	1.193(7)
O(4)	N(3)	1.218(7)
O(5)	N(3)	1.209(7)
O(6)	N(4)	1.204(9)
O(7)	N(4)	1.220(9)
N(1)	C(1)	1.468(8)
N(1)	C(2)	1.419(7)
N(1)	C(10)	1.381(7)
N(2)	C(3)	1.476(8)
N(3)	C(6)	1.487(8)
N(4)	C(8)	1.484(8)
C(2)	C(3)	1.452(8)
C(3)	C(4)	1.321(8)
C(4)	C(9)	1.434(8)
C(5)	C(6)	1.350(8)
C(5)	C(9)	1.396(8)
C(6)	C(7)	1.370(8)
C(7)	C(8)	1.361(8)
C(8)	C(10)	1.416(8)
C(9)	C(10)	1.408(8)

b Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Selected Torsion or Conformational Angles[c]

atom	atom	atom	atom	angle
O(3)	N(2)	C(3)	C(2)	- 159.3(8)
O(5)	N(3)	C(6)	C(7)	16 (1)
O(6)	N(4)	C(8)	C(7)	- 55(1)
N(1)	C(10)	C(8)	N(4)	- 15 (1)
C(1)	N(1)	C(2)	C(3)	- 170.8(7)
C(1)	N(1)	C(10)	C(8)	- 14 (1)
C(1)	N(1)	C(10)	C(9)	164.9(7)
C(2)	N(1)	C(10)	C(8)	172.7 (7)

c The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Table 4 Bond Angles and Distances for DNQ-Me

a

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

b

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

c

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Bond Angles Involving the Nonhydrogen Atoms[a]

atom	atom	atom	angle
C(1)	N(1)	C(2)	116.8(8)
C(1)	N(1)	C(10)	121.1(7)
C(2)	N(1)	C(10)	122.0(8)
O(1)	C(2)	N(1)	122.1(9)
N(1)	C(2)	C(3)	114.7(8)
O(1)	C(2)	C(3)	123.2(9)
C(2)	C(3)	C(4)	126.8(8)
N(2)	C(3)	C(2)	111.3(8)
N(2)	C(3)	C(4)	122.0(9)
O(2)	N(2)	C(3)	118 (1)
O(3)	N(2)	C(3)	117 (1)
O(2)	N(2)	O(3)	124 (1)
C(3)	C(4)	C(9)	115.3(9)
C(4)	C(9)	C(5)	117.6(9)
C(4)	C(9)	C(10)	122.1(9)
C(5)	C(9)	C(10)	120.3(8)
C(6)	C(5)	C(9)	117.3(9)
N(3)	C(6)	C(5)	120 (1)
N(3)	C(6)	C(7)	116.4(9)
O(4)	N(3)	C(6)	118.3(8)
O(5)	N(3)	C(6)	119.7(9)
O(4)	N(3)	O(5)	121.9(9)
C(5)	C(6)	C(7)	124 (1)
C(6)	C(7)	C(8)	119.2(9)
C(7)	C(8)	C(10)	120 (1)
C(8)	C(10)	C(9)	119.3(9)
N(1)	C(10)	C(9)	118.7(8)
N(1)	C(10)	C(8)	122.0(9)

atom	atom	atom	angle
C(1')	N(1')	C(2')	114.6(9)
C(1')	N(1')	C(10')	121.6(8)
C(2')	N(1')	C(10')	123.8(8)
O(1')	C(2')	N(1')	121.9(9)
N(1')	C(2')	C(3')	113.8(9)
O(1')	C(2')	C(3')	124.3(9)
C(2')	C(3')	C(4')	124.9(9)
N(2')	C(3')	C(2')	114.9(9)
N(2')	C(3')	C(4')	120 (1)
O(2')	N(2')	C(3')	118.7(9)
O(3')	N(2')	C(3')	116.6(9)
O(2')	N(2')	O(3')	124.7(9)
C(3')	C(4')	C(9')	119 (1)
C(4')	C(9')	C(5')	120.8(9)
C(4')	C(9')	C(10')	120 (1)
C(5')	C(9')	C(10')	118.9(9)
C(6')	C(5')	C(9')	119.1(9)
N(3')	C(6')	C(5')	119 (1)
N(3')	C(6')	C(7')	119.2(8)
O(4')	N(3')	C(6')	119.3(9)
O(5')	N(3')	C(6')	117 (1)
O(4')	N(3')	O(5')	123 (1)
C(5')	C(6')	C(7')	122.1(9)
C(6')	C(7')	C(8')	119.6(8)
C(7')	C(8')	C(10')	119.2(9)
C(8')	C(10')	C(9')	121 (1)
N(1')	C(10')	C(9')	118.3(8)
N(1')	C(10')	C(8')	120.6(9)

Bond Distances Involving the Nonhydrogen Atoms[b]

atom	atom	distance
N(1)	C(1)	1.50(1)
N(1)	C(2)	1.38(1)
O(1)	C(2)	1.22(1)
C(2)	C(3)	1.46(1)
N(2)	C(3)	1.49(1)
O(2)	N(2)	1.20(1)
O(3)	N(2)	1.22(1)
C(3)	C(4)	1.32(1)
C(4)	C(9)	1.44(1)
C(5)	C(9)	1.42(1)
C(5)	C(6)	1.37(1)
N(3)	C(6)	1.47(1)
O(4)	N(3)	1.24(1)
O(5)	N(3)	1.22(1)
C(6)	C(7)	1.37(1)
C(7)	C(8)	1.37(1)
C(8)	C(10)	1.41(1)
C(9)	C(10)	1.39(1)
N(1)	C(10)	1.41(1)

atom	atom	distance
N(1')	C(1')	1.49(1)
N(1')	C(2')	1.39(1)
O(1')	C(2')	1.21(1)
C(2')	C(3')	1.44(1)
N(2')	C(3')	1.46(1)
O(2')	N(2')	1.21(1)
O(3')	N(2')	1.236(9)
C(3')	C(4')	1.33(1)
C(4')	C(9')	1.42(1)
C(5')	C(9')	1.40(1)
C(5')	C(6')	1.37(1)
N(3')	C(6')	1.46(1)
O(4')	N(3')	1.22(1)
O(5')	N(3')	1.23(1)
C(6')	C(7')	1.39(1)
C(7')	C(8')	1.36(1)
C(8')	C(10')	1.41(1)
C(9')	C(10')	1.39(1)
N(1')	C(10')	1.41(1)

Selected Torsion or Conformational Angles[c]

atom	atom	atom	atom	angle
O(3)	N(2)	C(3)	C(2)	86(1)
O(5)	N(3)	C(6)	C(7)	22 (1)
C(1)	N(1)	C(2)	C(3)	174.5(9)
C(1)	N(1)	C(10)	C(8)	2 (1)
C(1)	N(1)	C(10)	C(9)	- 178(1)
C(2)	N(1)	C(10)	C(8)	- 176(1)
O(3')	N(2')	C(3')	C(2')	63(1)
O(5')	N(3')	C(6')	C(7')	- 17 (1)
C(1')	N(1')	C(2')	C(3')	- 176.9(9)
C(1')	N(1')	C(10')	C(8')	- 2 (1)
C(1')	N(1')	C(10')	C(9')	178(1)
C(2')	N(1')	C(10')	C(8')	179(1)

4-(2-Hydroxy-4-oxo-2-penten-3-yl)-1-methyl-6,8-dinitro-2-quinolone (3): Yellowish brown powder: mp 230-231 °C; IR (Nujol) 1684(br), 1541, 1346 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.93 (s, 6H), 3.83 (s, 3H), 6.80 (s, 1H), 7.57 (d, J = 9.3 Hz, 1H), 8.41 (d, J = 2.7 Hz, 1H), 8.47 (dd, J = 9.3, 2.7 Hz, 1H), 19.92 (s, 1H). Anal. Calcd for $C_{15}H_{14}N_2O_5$: C, 59.61; H, 4.66; N, 9.27. Found: C, 59.08; H, 4.53; N, 9.29.

REFERENCES

1. M. F. Grundon, *'The Alkaloids: Quinoline Alkaloids Related to Anthranic Acid,'* Vol. 32, Academic Press, London, 1988, p. 341.
2. For example; S. A. Barr, C. F. Neville, M. F. Grundon, D. R. Boyd, J. F. Malone, and T. A. Evance, *J. Chem. Soc., Perkin Trans. 1*, 1995, 445; S. A. Barr and D. R. Boyd, *J. Chem. Soc., Chem. Commun.*, 1994, 153; G. Brader, G. Wurz, and G. O. Hofer, *Liebigs Ann. Chem.*, 1993, 355.
3. K. C. Majumdar and A. K. Kundu, *Heterocycles*, 1997, **45**, 1467; A. E. Taubl and W. Stalbauer, *J. Heterocycl. Chem.*, 1997, **34**, 989; W. K. Anderson and D. K. Dalvie, *J. Heterocycl. Chem.*, 1993, **30**, 1533.
4. N. Nishiwaki, A. Tanaka, M. Uchida, Y. Tohda, and M. Ariga, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1377.
5. A. Kaufman and V. P. DePethard, *Ber.*, 1917, **50**, 336.
6. Y. Tohda, T. Katayama, T. Yanagitani, K. Imagawa, N. Nishiwaki, and M. Ariga, *Book of Abstracts 27th Congress of Heterocyclic Chemistry*, Morioka, Japan, Oct. 1996.
7. E. A. Prill, and S. M. McElvain, *Org. Synth.*, Coll. Vol. II, 1943, p. 419.
8. A. R. Katritzky and J. M. Lagowski, *'Chemistry of the Heterocyclic N-Oxides,'* Academic Press, London, 1971, p. 279.

Received, 28th October, 1998