SYNTHESIS AND STRUCTURE OF BROMONITRO-6(5H)-PHENANTHRIDINONES

A. M. Andrievskii, O. V. Chelysheva, A. N. Poplavskii,
V. V. Nikonov, L. A. Chetkina, V. K. Bel'skii,
V. E. Zavodnik, A. A. Perov, N. A. Andronova,
and K. M. Dyumaev

UDC 547.836.3.07;548.737:
543.422.25

Treatment of 2-bromo-6(5H)-phenanthridone with nitrating mixture or fuming nitric acid results in nitration, debromination, and bromination in the 10-position. The brominating agent is apparently Br$^+$, formed in the reaction mixture following replacement of the bromine in the 2-position by a nitro-group. Monocrystals of 2-bromo-1,4,8-trinitro-6(5H)-phenanthridinone and 10-bromo-2,4,8-trinitro-6(5H)-phenanthridinone have been subjected to x-ray diffraction examination. PMR has been used for structural identification.

During studies of the structural features of bromonitro-6(5H)-phenanthridinones by x-ray diffraction, it has been found that the compound previously regarded as 2-bromo-4,8,10-trinitro-6(5H)-phenanthridinone [1] is actually 10-bromo-2,4,8-trinitro-6(5H)-phenanthridinone (I). Since (I) was obtained by nitrating 2-bromo-6(5H)-phenanthridinone (II) with nitrating mixture, the presence of a bromine atom in the 10-position indicates that debromination–bromination has taken place. The isolation and identification of all the reaction products leads to the conclusion that the nitration follows two routes, in which the bromine in the 2-positon is either retained or is replaced by a nitro-group. Thus, on heating (II) with a mixture of nitric (d 1.51) and sulfuric (d 1.83) acids at 95°C for 2 h there were obtained: 2-bromo-1,4,8-trinitro-6(5H)-phenanthridinone (III) (48%), (I) (21%), 2,10-dibromo-1,4,8-trinitro-6(5H)-phenanthridinone (IV) (7%), and 2,4,8,10-tetranitro-6(5H)-phenanthridinone (V) (11%) (see scheme below).

TABLE 1. Properties of Bromonitro-6(5H)-phenanthridinones (I), (III), (IV), (VI), and (VIII)

Compound	Empirical formula	mp, °C	R^*_f	IR spectrum, ν, cm^{-1}			M^+
				C=O	NO_2	NH	
I	$C_{13}H_5BrN_4O_7$	226...228	0,56	1700	1350, 1540	3100, 3260	408
III	$C_{13}H_5BrN_4O_7$	244	0,86	1690	1340, 1540	3090, 3250	—
IV	$C_{13}H_4Br_2N_4O_7$	251...252	0,89	1700	1360, 1560	—	488
VI	$C_{13}H_6BrN_3O_5$	302...303	0,79	1700	1340, 1530	3100, 3240	363
VIII	$C_{13}H_7BrN_2O_3$	278...278,5 (282...284 [2])	0,76	1670	1350, 1530	3090, 3350	319

*In a mixture of acetone and benzene (1:7).

Research Institute for Organic Intermediates and Dyes, Moscow 103787. L. Ya. Karpov Research Institute for Physical Chemistry, Moscow 103064. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 789-795, June, 1990. Original article submitted March 21, 1988; revision submitted September 15, 1988.

0009-3122/90/2606-0658$12.50

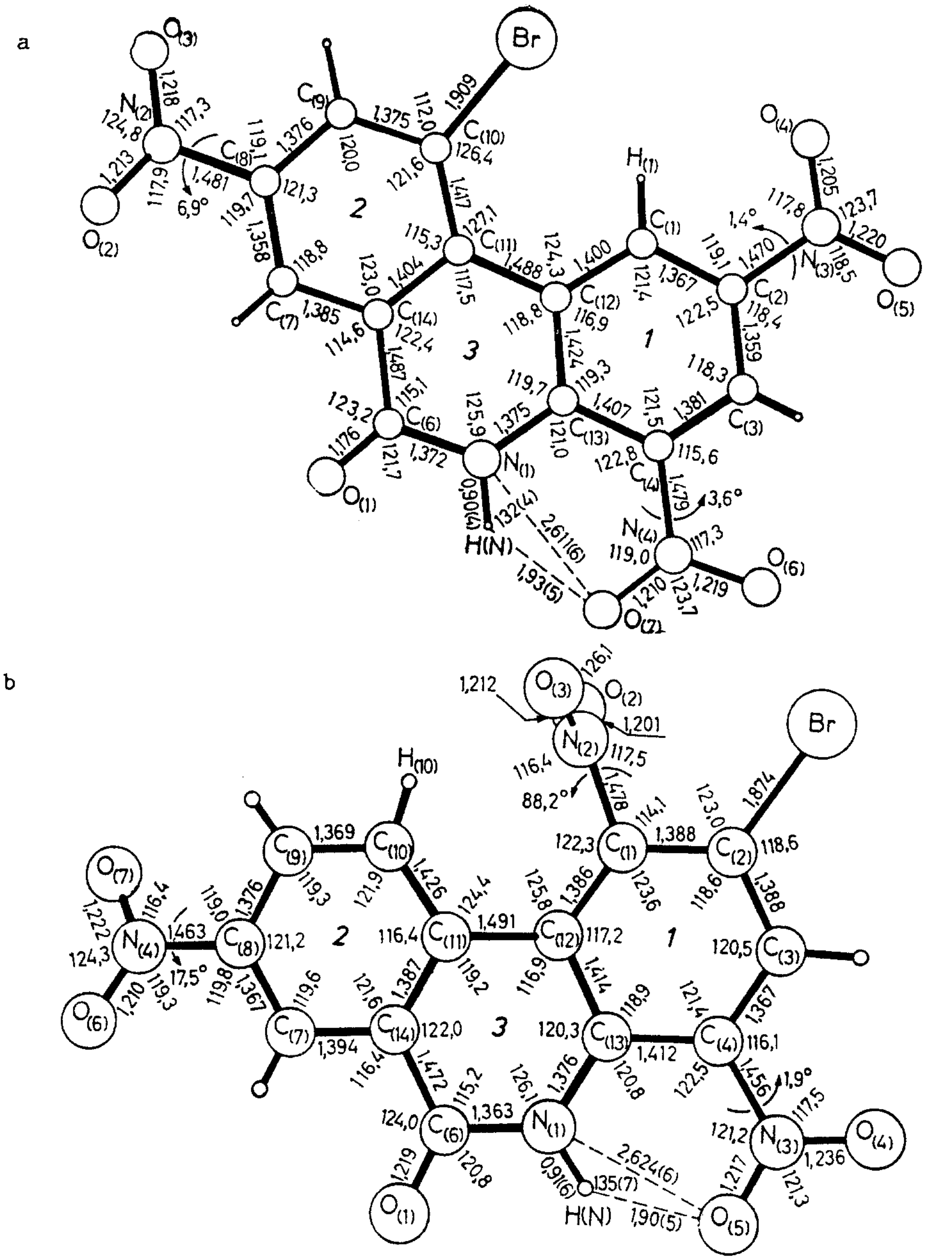
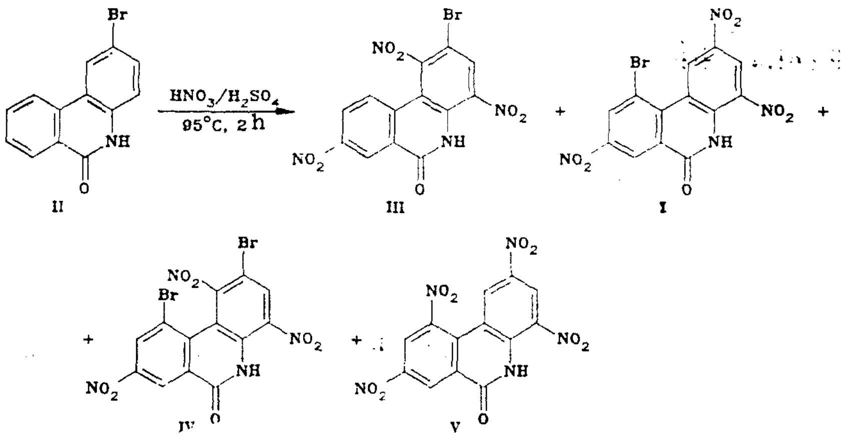


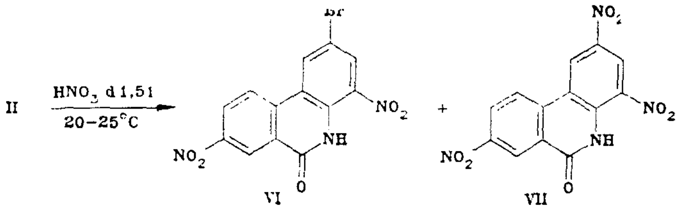
Fig. 1. Geometry of the molecules of (I) (a) and (III) (b), with the rotation angles of the nitro-groups.

TABLE 2. PMR Spectra of Bromonitro-6(5H)-phenanthridinones (IV), (VI), and (VIII)

Compound	Chemical shift, δ, ppm (DMSO-D_6)						
	1-H	3-H	7-H	8-H	9-H	10-H	NH
IV	—	8,00	8,63		8,80	—	10,51
VI	8,54	8,89	9,10	—	8,60	8,90	10,96
VIII	8,48	9,09	8,71	7,95	7,78	8,34	11,06

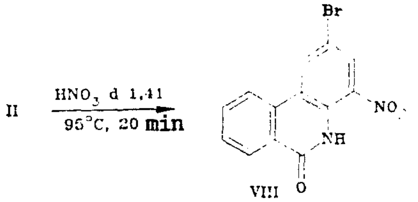


Treatment of (II) with nitric acid (d 1.51) at 20°C gave 2-bromo-4,8-dinitro-6(5H)-phenanthridinone (VI) and 2,4,8-trinitro-6(5H)-phenanthridinone (VII). As time progressed, the amount of (VI) in the reaction mixture decreased, and that of the trinitro-compound (VII) increased. When sulfuric acid (d 1.83) was added to this mixture and the temperature raised to 95°C for 2 h, the same products were obtained as when (II) was treated with nitrating mixture (Table 1).



It is likely that, in the initially-formed bromo-nitro compound (VI), in addition to replacement of the bromine atom by a nitro-group to give (VII), further nitration to (III) occurs. Bromination of (VII) and (III) takes place simultaneously to give (I) and (IV), respectively. The brominating agent is evidently Br$^+$, formed in the reaction mixture following replacement of Br$_{(2)}$ by a nitro-group. Bromination only occurs in the presence of sulfuric acid, so that in nitric acid (d 1.51) the reaction stops with the formation of (VI) and (VII).

Under milder conditions, namely treatment of (II) with nitric acid (d 1.41), nitration occur only in the 4-position to give the previously reported [2] 2-bromo-4-nitro-6(5H)-phenanthridinone (VIII). On treatment with fuming nitric acid or nitrating mixture, this compound gives the same product as are obtained with (II).



The positions of the substituents in (I) and (III) were established by x-ray diffraction examination, the structures of (IV), (VI), and (VIII) being determined from their PMR spectra.

In the molecules of (I) and (III), the standard deviations of the C–Br bond lengths were 0.005, of C–C, C–N, and C–O 0.006-0.007, and of N–O 0.005-0.007 Å, of the CCBr valence angles 0.3°, and of the other nonhydrogen atoms 0.4-0.5° (Fig. 1).

The geometry of the phenanthridinone ring in the isomeric molecules (I) and (III) was in agreement with that previously found for (V) [3] and 10-acetoxy-2,4,8-trinitro-6(5H)-phenanthridinone (IX) [4], differing from those in the unsubstituted 6(5H)-phenanthridinone (X) [5] and 4-nitro-6(5H)-phenanthridinone (XI) [6]. Electron-acceptor substituents result in an increase in the endocyclic CC(N)C angles by an average of 1.7° (I) or 2.1° (III), as compared with the angles in (X) and (XI), in which they are ~120°, and in distortion of the planarity of the phenanthridinone ring. The maximum departure (Δ_{max}) of the atoms from the mean plane of the tricyclic system (atoms N$_{(1)}$, C$_{(1)}$–C$_{(13)}$) were 0.143 Å [in (I)] and 0.096 Å [in (III)], the molecule of (X) being planar to within 0.05 Å [5], and that of (XI) to within 0.057 Å [6]. The individual rings were more planar. For ring 1 (Fig. 1), Δ_{max} was 0.019 Å [in (I)] and 0.018 Å [in (III)], for ring 2, 0.011 Å (I) and 0.007 Å (III), and for ring 3, 0.055 Å (I) and 0.031 Å (III). Atom $O_{(1)}$ departs from plane 3 by –0.159 Å in (I) and –0.113 Å in (III). The dihedral angles between planes 1 and 2 are 9.7° (I) and 6.0° (III), planes 1 and 3, 4.2° (I) and 4.6° (III), and planes 2 and 3, 6.5° (I) and 3.1° (III).

In the molecule of (I), the steric hindrance between $H_{(1)}$ and Br (Fig. 1) results in an increase in the exocyclic valence angles $BrC_{(10)}C_{(11)}$, $C_{(10)}C_{(11)}C_{(12)}$, and $C_{(1)}C_{(12)}C_{(11)}$,thisdeformation being greater than that in (V) [3]. When no substituent is present in the 1 and 10 positions, the external valence angles are 122-123° [6]. The nonvalent Br...$H_{(1)}$ distance [2.43(2) Å] remains much shorter than the sum of the van der Waals radii, which is 3.13 Å. In (IX) and 10-hydroxy-2,4,8-trinitro-6(5H)-phenanthridinone, x-ray and PMR studies have demonstrated intramolecular hydrogen bonding (IHB) between $H_{(1)}$ in ring 1 and the oxygen of the acetoxy (or hydroxy) group in the 10-position [4]. By analogy, it may be assumed that C–H...Br hydrogen bonding is also present in (I). In the heterocycle of (I), the bond length $C_{(6)}–C_{(14)}$ is increased to 1.487 Å [1.472 in (III), 1.469 in (V), 1.470 in (IX), and 1.454 in (XI)], and C=O is shortened to 1.176 Å [the standard $C(sp^2)=O$ bond length is 1.219 Å]. This is probably due to the influence of the bromine atom, transmitted along the $C_{(10)}–C_{(11)}–C_{(14)}–C_{(6)}=O_{(1)}$ chain. The bromine atom lies in the plane of its ring, with $\Delta = -0.014$ Å.

The conformation of (III) is determined by more complex steric factors, and the electronic influence of the ortho- and meta-nitro-groups relative to $Br_{(2)}$ (Fig. 1b). The rotation angle of the NO_2 group in the 1-position (88.2°) is the highest which has so far been reported: in (V) this angle (for the 10-position) is 65.7° [3], the maximum angle in polynitrophenanthridinones 68.5° [7], and polynitrodibenzopyranones 65.8° [8], while in the sterically greatly overloaded benzene derivatives these angles are 76.1-84.7° [9]. The nonvalent $H_{(10)}$...$N_{(2)}$ distance is 2.34(5) Å, which is less than the sum of the van der Waals radii, 2.66 Å [in (V), $N_{(5)}$...$H_{(1)}$ is 2.21 Å]. The Br atom in (III) departs from plane 1 by –0.105 Å (the angle of inclination of the $C_{(2)}$–Br bond is 3.2°).

The C–Br bond lengths in (I) and (III) are similar, differing little from the standard value of 1.88 Å [10], and from those found in bromoaromatic compounds [11, 12]. The conformation of the molecule in (I) and (III) is also characterized by IHB between the imino-group of the heterocycle and an oxygen of the adjacent nitro-group. The parameters of this bond are shown in Fig. 1. Similar IHB is also found in other nitrophenanthridinones with a nitro-group in the 4-position: the length of the N...O hydrogen bond in (V) is 2.615 Å [3], 2.640 Å in (IX) [4], and 2.664 Å in (XI) [6].

The packing of the molecules in (III) results in a shortened intermolecular contact Br(x, y, z)...$O_{(4)}$ (1 – x, –0.5 + y, –z) of 2.967(5) Å. This distance is less than the sum of the van der Waals radii (3.37 Å) of these atoms, and according to [13] is less than the upper limit (3.04 Å) for specific intermolecular interactions. The value of the $C_{(2)}BrO_{(4)}'$ angle, 171.1 (3°), indicates the directional nature of the specific interaction. This interaction is probably attributable to a slight decrease in the $C_{(2)}$–Br bond length, and an increase in $N_{(3)}–O_{(4)}$.

Assignments of the signals in the PMR spectra of (IV), (VI), and (VIII) (Table 2) were made on the basis of the multiplicity of the signals, taking into account the influence of the nitro-groups on the aromatic protons. Successive replacement of protons by nitro-groups results in simplification of the spectra for the aromatic protons. Introduction of a nitro-group into the 4-position (in VIII) results in a separation of the signals as two doublets from the protons in the 1- and 3-positions, with m-coupling constants. The signals for the 7- and 10-protons are seen as quartets, and those for the 8- and 9-protons as multiplets. The coupling constants of the protons are typical of nitrophenanthridinones [1], with o-constants of ~8.3, and m-constants ~2 Hz. In (VI), the signals for the 1-H and 3-H protons are also seen as two doublets with an m-constant. The signals for the 7-H, 9-H, and 10-H protons give rise to a characteristic ABC system in the spectrum. This is shown by the occurrence of a doublet with an m-coupling constant for 7-H, doublet with an o-constant for 10H, and a quartet for 9-H. The spectrum also shows partial overlapping of the signals for the 3-H and 10-H protons. The proton in the 3-position in (IV) is seen as a clear singlet, the 7-H and 8-H protons appearing as two doublets. The chemical shifts of the NH protons in (IV), (VI), and (VIII) lie in the range 10.5-11.0 ppm.

EXPERIMENTAL

IR spectra were obtained on a Perkin–Elmer 580 spectrometer in KCl disks. The PMR spectrum of a saturated solution of (IV) in DMSO-D_6 (isotope content 99.3%) was obtained on a Tesla BS-467 spectrometer at 20°C in normal mode (internal standard HMDS). The accuracy of measurement of the chemical shifts was ±0.05 ppm. The PMR spectra of (VI) and (VIII) were obtained in the same solvent on a Bruker AM-400 spectrometer in impulse accumulation mode at 40°C (internal standard TMS), accuracy of measurement of chemical shifts ±0.001 ppm.

Mass spectra were obtained by the field desorption method on a Varian MAT-731 mass spectrometer. The purity of the products was checked by TLC on Silufol UV-254 plates in the system acetone–benzene, 1:7. The products were separated from the reaction mixtures on a column (3 × 100 cm) of Silicagel L 100/160, eluent benzene.

TABLE 3. Atom Coordinates for Br (× 10^5), O, N, C (× 10^4), and H(N) (× 10^3), and Equivalent Isotropic Temperature Factors [for H(N), U_{iso}] ($Å^2 \times 10^3$)

Atom	Compound	*x*	*y*	*z*	U_{iso}equiv
Br	I	9659(3)	30115(3)	53366(7)	54,8(4)
	III	58096(3)	50000	11584(7)	53,1(2)
$O_{(1)}$	I	1735(2)	4895(2)	239(4)	53(2)
	III	6697(2)	9113(2)	9242(5)	53(1)
$O_{(2)}$	I	2047(2)	4010(2)	8519(5)	81(3)
	III	6623(3)	4665(3)	6074(6)	67(2)
$O_{(3)}$	I	2768(2)	4793(2)	8860(5)	73(3)
	III	7752(3)	5047(4)	4129(5)	72(1)
$O_{(4)}$	I	3474(2)	6087(2)	5041(5)	58(2)
	III	4798(3)	8319(3)	914(7)	63(2)
$O_{(5)}$	I	3127(1)	5930(1)	2881(4)	43(2)
	III	5339(3)	9119(3)	3389(6)	59(1)
$O_{(6)}$	I	290(2)	3096(2)	−1181(5)	75(3)
	III	8794(3)	7713(3)	14262(6)	73(2)
$O_{(7)}$	I	52(2)	2406(2)	262(6)	68(3)
	III	9559(3)	6567(3)	13206(8)	90(2)
$N_{(1)}$	I	2192(2)	5038(2)	2339(4)	36(2)
	III	6298(3)	8358(3)	6354(6)	37(1)
$N_{(2)}$	I	2387(2)	4462(2)	8103(5)	54(3)
	III	7019(3)	5177(3)	4945(6)	43(1)
$N_{(3)}$	I	3124(2)	5799(2)	4148(4)	35(2)
	III	5262(3)	8398(3)	2511(7)	43(1)
$N_{(4)}$	I	319(2)	2893(2)	−33(5)	50(2)
	III	8935(3)	7107(3)	13045(7)	48(2)
$C_{(1)}$	I	1915(2)	4245(2)	5745(6)	40(3)
	III	6576(3)	6049(3)	4490(6)	30(1)
$C_{(2)}$	I	2339(2)	4619(2)	6596(5)	37(3)
	III	6032(3)	6042(4)	2723(7)	36(1)
$C_{(3)}$	I	2729(2)	5118(2)	6079(5)	38(3)
	III	5615(3)	6832(4)	2129(7)	37(2)
$C_{(4)}$	I	2681(2)	5255(2)	4653(5)	31(2)
	III	5726(3)	7598(4)	3281(7)	36(1)
$C_{(6)}$	I	1779(2)	4721(2)	1373(5)	40(2)
	III	6752(3)	8431(3)	8197(7)	35(1)
$C_{(7)}$	I	1052(2)	3802(2)	773(6)	38(2)
	III	7815(3)	7716(3)	10594(7)	34(1)
$C_{(8)}$	I	705(2)	3265(2)	1098(2)	39(2)
	III	8346(3)	7010(4)	11222(7)	35(2)
$C_{(9)}$	I	704(2)	3055(2)	2464(5)	38(2)
	III	8359(3)	6213(4)	10133(8)	42(2)
$C_{(10)}$	I	1051(2)	3396(2)	3540(5)	36(2)
	III	7845(4)	6134(4)	8363(8)	40(2)
$C_{(11)}$	I	1428(2)	3959(2)	3267(5)	32(2)
	III	7281(3)	6849(3)	7633(6)	30(1)
$C_{(12)}$	I	1857(2)	4359(2)	4282(5)	30(2)
	III	6712(3)	6805(3)	5714(7)	27(1)
$C_{(13)}$	I	2247(2)	4890(2)	3740(5)	30(2)
	III	6254(3)	7602(3)	5118(7)	30(1)
$C_{(14)}$	I	1406(2)	4144(2)	1851(5)	33(2)
	III	7285(3)	7633(3)	8804(6)	32(2)
H(N)	I	244(2)	538(2)	204(5)	42(15)
	III	599(3)	885(4)	587(8)	60(19)

The x-ray diffraction examination was carried out on Nicolet R-3 (I) and Syntex PT diffractometers (III). Monocrystals of the isomers (I) and (III) were grown from solutions in acetic acid, M = 409.1 ($C_{13}H_{15}N_4O_7Br$). The crystals of (I) were trigonal, with *a* = b = 28.057(5), c = 9.116(2) Å, V = 6214(2) $Å^3$, sp. grp. R 3, Z = 18, d_{calc} = 1.967 g/cm^3. The crystals of (III) were rhombic, with *a* = 14.665(3), b = 14.858(3), c = 6.426(1) Å, V = 1400.4(6) $Å^3$, sp. grp. Pb2$_1$*a*, Z = 4, d_{calc} = 1.940 g/cm^3. The intensities of 1593 (I) and 950 (III) independent reflections with $I \geq 3\sigma$ (I) were obtained with Mo Kα irradiation, $\theta/2\theta$ scanning to $2\theta_{max} = 55°$ (I) and 48° (III), a correction for absorption being made in the case of (III). The structures were calculated directly, and refined by least squares in full-matrix anisotropic approximation for the O, N, C, and Br atoms, and isotropic approximation for the H atoms, to R factors of 0.040 (I) and 0.021 (III) (Table 3). All calculations were carried out using the SHELXTL programs of the Nicolet R-3 system on a NOVA-3 minicomputer.

The elemental analysis of the compounds for C, H, N, and Br were in agreement with the calculated values.

2,10-Dibromo-1,4,8-trinitro-6(5H)-phenanthridinone (IV), 2-Bromo-1,4,8-trinitro-6(5H)-phenanthridinone (III), 10-Bromo-2,4,8-trinitro-6(5H)-phenanthridinone (I), and 2,4,8,10-Tetranitro-6(5H)-phenanthridinone (V). To a mixture of 5 ml of nitric acid (d 1.51) and 30 ml of sulfuric acid (d 1.83) was added 1.37 g (5 mmoles) of (II), and the mixture stirred for 2 h at 95°C, cooled, and poured onto 200 g of ice. The solid was filtered off, washed with 50 ml of water, and dried to give 1.87 g of nitration products. The mixture was dissolved in 150 ml of benzene, applied to a column of silica gel, and eluted with benzene. From the first fraction there was obtained 0.17 g (7%) of (IV) as yellow crystals from acetic acid. The second fraction gave 0.98 g (48%) of (III), the third fraction 0.43 g (21%) of (I), and the fourth fraction 0.2 g (11%) of (V).

2-Bromo-4,8-dinitro-6(5H)-phenanthridinone (VI) and 2,4,8-Trinitro-6(5H)-phenanthridinone (VII). To 20 ml of nitric acid (d 1.51) was added 1.37 g (5 mmoles) of (II), the mixture stirred at 20°C for 30 min, and the solution poured onto 150 g of ice. The solid was filtered off, washed with 50 ml of water, and dried. The mixture (1.64 g) was dissolved in 200 ml of benzene, and eluted from a column of silica gel with benzene. From the first fraction there was obtained 0.96 g (53%) of (VI) as bright yellow crystals from acetic acid and, from the second, 0.48 g (29%) of (VII), identical to a sample obtained as in [1] in respect of its R_f value, IR spectrum, and melting point.

2-Bromo-4-nitro-6(5H)-phenanthridinone (VIII). To 50 ml of nitric acid (d 1.41) was added 1.37 g (5 mmoles) of (II), and the mixture stirred at 95°C for 20 min, cooled, and poured onto 200 g of ice. The solid was filtered off, washed with water, and twice recrystallized from acetic acid to give 1.31 g (82.4%) of (VIII) as bright yellow crystals.

We thank A. N. Sobolev for assistance in calculating the structure of (III).

LITERATURE CITED

1. A. M. Andrievskii, A. N. Poplavskii, K. M. Dyumaev, Yu. S. Bogachev, and S. S. Berestova, *Khim. Geterotsikl. Soedin.*, No. 8, 1106 (1985).
2. H. Gilman and J. Eisch, *J. Am. Chem. Soc.* **79**, 5479 (1957).
3. L. A. Chetkina, Z. P. Povet'eva, V. K. Bel'skii, A. M. Andrievskii, A. N. Poplavskii, and K. M. Dyumaev, *Dokl. Akad. Nauk SSSR* **266**, 1191 (1982).
4. A. M. Andrievskii, A. N. Poplavskii, K. M. Dyumaev, L. A. Chetkina, V. K. Bel'skii, Yu. S. Bogachev, and S. S. Berestova, *Khim. Geterotsikl. Soedin.*, No. 3, 314 (1987).
5. D. K. Sen, *J. Cryst. Mol. Struct.* **6**, 153 (1976).
6. L. A. Chetkina, O. V. Semidetko, V. A. Shuvaeva, A. N. Poplavskii, V. K. Bel'skii, and A. M. Andrievskii, *Zh. Strukt. Khim.* **28**, 177 (1987).
7. O. V. Semidetko, L. A. Chetkina, V. K. Bel'skii, A. M. Andrievskii, A. N. Poplavskii, and K. M. Dyumaev, *Kristallografiya* **34**, 106 (1988).
8. L. A. Chetkina, E. G. Popova, V. K. Bel'skii, A. M. Andrievskii, A. N. Poplavskii, and K. M. Dyumaev, *Dokl. Akad. Nauk SSSR* **285**, 1160 (1985).
9. K. Padmanabhan, V. Ramamurthy, and K. Venkatesan, *Acta Cryst.* **C42**, 610 (1986).
10. S. S. Batsanov, *Experimental Fundamentals of Structural Chemistry* [in Russian], Izd-vo Standartov, Moscow (1986), p. 66.
11. J. Silverman, A. P. Krukonis, and N. F. Yannoni, *Acta Cryst.* **B29**, 2022 (1973).
12. E. K. Corey, *Acta Cryst.* **B35**, 201 (1979).
13. Yu. V. Zefirov and M. A. Porai-Koshits, *Zh. Strukt. Khim.* **27**, 74 (1986).