Organic Chemistry

Effect of the solvent nature and the number of electrophilic substituents in the molecule on hydration of nitro derivatives of phenanthrene-9,10-quinone

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Solvates (1 : 2) of 10,10-dihydroxy-2,4,7-trinitro-9,10-dihydrophenanthren-9-one with DMSO and of 10,10-dihydroxy-2,7-dinitro-9,10-dihydrophenanthren-9-one with HMPA were prepared. The crystal structure of 2,5-dinitrophenanthrene-9,10-quinone was established. The results of X-ray diffraction analysis and IR spectroscopy of a series of mono-, di-, and trinitro derivatives of phenanthrene-9,10-quinone demonstrated that the ability of carbonyl groups to participate in nucleophilic addition of water increases as the number of nitro groups in substituted phenanthrene-9,10-quinone increases. The nature of the solvent (HMPA, DMF, or DMSO) affects hydration of phenanthrenequinones primarily due to the difference in the strength of intermolecular hydrogen bonds stabilizing di- and tetrahydroxydihydrophenanthrenes.

Key words: 10,10-dihydroxy-2,4,7-trinitro-9,10-dihydrophenanthren-9-one, 10,10-dihydroxy-2,7-dinitro-9,10-dihydrophenanthren-9-one, 2,5-dinitrophenanthrene-9,10-quinone, hydration, solvate, X-ray diffraction study, IR spectroscopy.

The chemical and physicochemical properties of phenantherene-9,10-quinone and its derivatives are poorly studied, which prevents practical use of these compounds. Therefore, detailed studies of their properties and structures is a topical problem of synthetic and physical chemistry. Nitro-substituted phenanthrene-9,10-quinones can be used as precursors for various derivatives. Previously, it has been demonstrated[1,2] that the character of hydration of 2,4,7-trinitrophenanthrene-9,10-quinone (**1**) and 4-bromo-2,7-dinitrophenanthrene-9,10-quinone (**2**) (Scheme 1) depends on the nature of the solvent. The structures of the resulting compounds (**3**—**5**) were established by X-ray diffraction analysis.

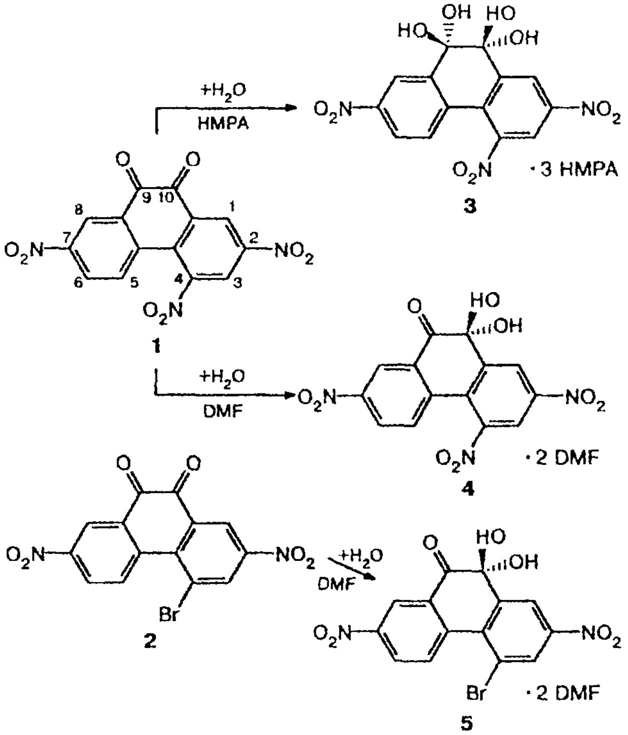
In this work, we studied hydration of 2,7-dinitro-, 2,5-dinitro-, 4-nitro-, and 2-nitrophenanthrene-9,10-quinone (**6**—**9**, respectively) in DMF, compound **1** in DMSO, and compounds **6** and **9** in HMPA.

Results and Discussion

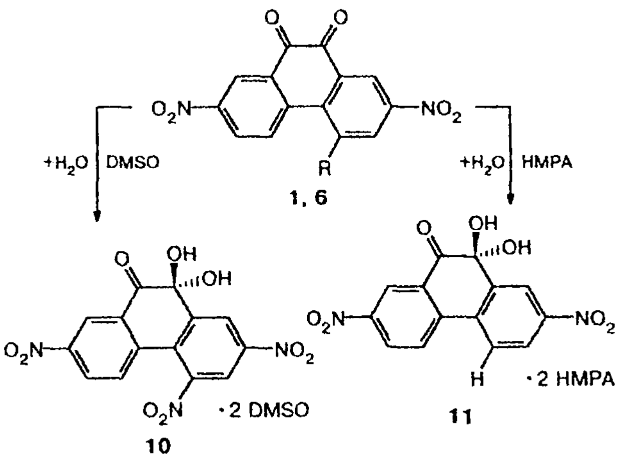
2,4,7-Trinitrophenanthrene-9,10-quinone (**1**) dissolved in DMSO or in DMF added one molecule of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 738—742, April, 1999.

Scheme 1



Scheme 2



water to form compound **10**, which was isolated as a solvate with composition 1 : 2 (Scheme 2).

The addition of a molecule of water only at one C=O group is evidenced by the fact that the IR spectrum of compound **10** has both a broad ν(OH) band overlapping with ν(C$_{Ar}$—H) and ν(CH$_3$) bands and a ν(C=O) band shifted to the high-frequency region compared to the initial compound **1** by 36 cm^{-1} (Table 1). The IR spectrum of compound **10** is similar to those of hydrates **4** and **5** whose structures were established by X-ray diffraction analysis,[1,2] which suggests that in the case under consideration hydration occurred also at the C(10)=O group.

The composition of the solvate was confirmed by the data of elemental analysis and by the fact that its IR spectrum has ν(S=O) bands at 1008 cm^{-1}. The low-frequency shift of the ν(S=O) bands compared to the band of free DMSO (1070 cm^{-1})[3] is due to the participation of DMSO molecules in the formation of intermolecular O—H...O=S hydrogen bonds. The function of the DMSO molecules of solvation is to stabilize the hydrate through intermolecular hydrogen bonding. This is also evidenced by the fact that in a CCl$_4$ solution the intermolecular hydrogen bonds are broken and compound **10** is dehydrated to form the initial compound **1**. Actually, the intensities of the bands at 3635 cm^{-1} (ν(OH) of free OH groups) and 1730 cm^{-1} (ν(C=O)) observed in the IR spectrum of a freshly prepared solution of **10** decrease with time, while the intensity of the band at 1700 cm^{-1} (ν(C=O) of compound **1**) increases.

Of the remaining compounds under study, only 2,7-dinitrophenanthrene-9,10-quinone (**6**) underwent hydration. The fact that the molecule of compound **6** in HMPA adds a water molecule only at one C=O group is confirmed by the presence of both ν(C=O) and ν(OH) bands in the IR spectrum of solvate **11** (see Table 1). The fact that two solvent molecules are incorporated in the crystal solvate is confirmed by the data of elemental analysis and by the presence of ν(P=O) (1196 cm^{-1}) and ν(CH$_3$) (2920, 2888, and 2848 cm^{-1}) bands in the IR spectrum of the compound under study. It should also be noted that this compound is unstable even in the crystalline state. Storage of this compound under re-

Table 1. Selected bands in the IR spectra of compounds **1—11** (KCl pellets)

Compound	ν/cm^{-1}				
	OH*	C=O	NO$_2$, as	NO$_2$, s	X=O**
1		1718 w, 1700	1536, 1518	1348	
2		1712 w, 1695	1520	1344	
3	3600—2800		1533, 1517	1342	1197 (P)
4	3200—2600	1740	1540, 1526	1350	1660 (C)
5	3300—2000	1740	1524	1346	1658 (C)
6		1682	1518	1360	
7		1696	1536, 1520	1342	
8		1690	1528	1366	
9		1674	1522	1344	
10	3550—2600	1736	1540, 1526	1350	1008 (S)
11	3600—2700	1724	1524	1348	1196 (P)

* An intense broad band overlapping with ν(C$_{Ar}$—H) and ν(CH$_3$).

** Stretching vibrations of the C=O, S=O, and P=O groups of the DMF, DMSO, and HMPA molecules of solvation, respectively.

duced pressure led to a gradual loss of solvate HMPA molecules and dehydration. This is evidenced by a decrease in the intensities of stretching vibration bands of the C=O, OH, CH_3, and P=O groups in the IR spectrum of solvate **11** with the simultaneous appearance of a ν(C=O) band of the initial quinone **6** (1682 cm^{-1}) followed by an increase in its intensity.

Of the phenanthrene-9,10-quinone derivatives under study, only compounds **1** and **2** were hydrated in DMF and hydration occurred only at the C(10)=O bond. In this connection, it was of interest to establish the crystal structure of 2,5-dinitrophenanthrene-9,10-quinone (**7**) with the aim of revealing the relationship between the structural characteristics of the compounds under study and their reactivity.

The structure of molecule **7** is shown in Fig. 1. The geometric parameters of molecule **7** (Tables 2 and 3) are typical of a series of compounds studied previously.[4,5] The molecular geometry, bond lengths, and bond angles in the structure of **7** are the closest to those observed in trinitrophenanthrenequinone **1**.[5] Unlike nonsubstituted phenanthrene-9,10-quinone[4] and like compound **1**, molecule **7** is somewhat nonplanar and exhibits typical distortions due to the presence of the O atoms of the carbonyl groups and nitro groups that cause steric hindrances. In the *ortho*-quinone fragment of **7**, as in compound **1** and phenanthrene-9,10-quinone, the nonbonded interactions of the O atoms lead to the increase in the C(9)—C(10) bond (1.523(2) Å) compared to the standard $C(sp^2)$—$C(sp^2)$ bond length (1.479 Å).[6] The O atoms deviate from the mean plane of the central ring of molecule **7** in opposite directions by −0.276 and +0.388 Å, respectively, *i.e.*, these deviations are larger than those in **1** (−0.252 and +0.259 Å). In this case, the O(1)...O(2) distance (2.752(2) Å) remains shorter than the normal van der Waals O...O contact[7] (2.8 Å). The C=O bond lengths (1.209(2) and 1.214(2) Å) coincide with the corresponding values in other related compounds, including the structure of **1** [5] (1.208 and 1.213 Å) and phenanthrene-9,10-quinone[4] (1.210 and 1.212 Å). The bond angles at the C(9) and C(10) atoms also coincide with those observed previously. However, the O(1)...H(8) (2.505 Å) and O(2)...H(1) (2.519 Å) contacts remain shortened (the normal van der Waals O...H contact is 2.6 Å).[7]

The two nitro groups are in different positions with respect to the mean plane of molecule **7**. The nitro group at position 2 virtually does not experience steric hindrances and lies nearly in the plane of ring *A* (the angle between the plane of NO_2 and the mean plane of ring *A* is 5.3(2)°). The second nitro group at position 5 is forced to be rotated with respect to the mean plane of ring *B* by 47° due to shortened contacts with the H atoms at the C(4) and C(6) atoms (in molecule **1**, the nitro groups at positions 7 and 4 are rotated by 15.7 and 59.7°, respectively). In this case, both nitro groups have similar geometric characteristics, which are close to the standard values.[8] The steric strain caused by the attachment of the NO_2 group at position 5 is manifested not only in the substantial increase in the lengths of all the bonds in the C(4)—C(12)—C(13)—C(5) chain but also in the increase in the exocyclic angles at the same C atoms. In spite of the above-described distortions, the N(2)...C(4) (2.976 Å), N(2)...C(6) (2.400 Å), N(2)...H(4) (2.44 Å), N(2)...H(6) (2.51 Å), O(5)...C(4) (2.837 Å), and O(6)...C(6) (2.752 Å) contacts are substantially smaller than the sums of the corresponding van der Waals radii (3.20, 2.70, and 3.10 Å, respectively[7]).

As mentioned above, the tricyclic system in molecule **7** is somewhat nonplanar. The central ring *C* adopts a distorted boat conformation. The C(9) and C(12) atoms deviate from the plane through the remaining four atoms C(10)C(11)C(13)C(14) (planar to within ±0.05 Å) in the same direction by 0.198 and 0.178 Å, respectively. Benzene rings *A* and *B* are virtually planar. The average deviation in ring *A* is ±0.012 Å. In ring *B*, this value is somewhat larger (±0.026 Å). The dihedral angles between rings *A* and *B*, *A* and *C*, and *B* and *C* are 22, 14, and 10°, respectively.

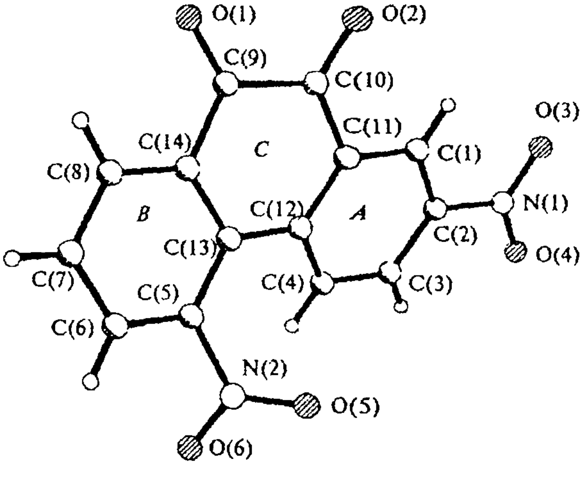


Fig. 1. Molecular structure of compound **7**.

Table 2. Bond lengths (*d*) in the structure of **7**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(9)	1.209(2)	C(4)—C(12)	1.400(2)
O(2)—C(10)	1.214(2)	C(5)—C(6)	1.383(3)
O(3)—N(1)	1.217(2)	C(5)—C(13)	1.405(2)
O(4)—N(1)	1.211(2)	C(6)—C(7)	1.379(3)
O(5)—N(2)	1.215(2)	C(7)—C(8)	1.383(3)
O(6)—N(2)	1.227(2)	C(8)—C(14)	1.392(3)
N(1)—C(2)	1.471(2)	C(9)—C(14)	1.479(2)
N(2)—C(5)	1.477(2)	C(9)—C(10)	1.523(3)
C(1)—C(2)	1.370(2)	C(10)—C(11)	1.475(2)
C(1)—C(11)	1.391(3)	C(11)—C(12)	1.408(2)
C(2)—C(3)	1.382(2)	C(12)—C(13)	1.484(2)
C(3)—C(4)	1.377(3)	C(13)—C(14)	1.411(2)

Table 3. Bond angles (ω) in the structure of **7**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(4)—N(1)—O(3)	123.6(2)	C(6)—C(5)—C(13)	123.6(2)	C(1)—C(11)—C(12)	121.6(2)
O(4)—N(1)—C(2)	118.5(2)	C(6)—C(5)—N(2)	114.1(2)	C(1)—C(11)—C(10)	117.57(14)
O(3)—N(1)—C(2)	117.8(2)	C(13)—C(5)—N(2)	122.1(2)	C(12)—C(11)—C(10)	120.5(2)
O(5)—N(2)—O(6)	124.6(2)	C(7)—C(6)—C(5)	119.9(2)	C(4)—C(12)—C(11)	117.3(2)
O(5)—N(2)—C(5)	118.7(2)	C(6)—C(7)—C(8)	119.2(2)	C(4)—C(12)—C(13)	122.97(14)
O(6)—N(2)—C(5)	116.5(2)	C(7)—C(8)—C(14)	120.3(2)	C(11)—C(12)—C(13)	119.67(14)
C(2)—C(1)—C(11)	118.1(2)	O(1)—C(9)—C(14)	123.3(2)	C(5)—C(13)—C(14)	114.4(2)
C(1)—C(2)—C(3)	122.2(2)	O(1)—C(9)—C(10)	119.2(2)	C(5)—C(13)—C(12)	125.83(14)
C(1)—C(2)—N(1)	118.5(2)	C(14)—C(9)—C(10)	117.49(14)	C(14)—C(13)—C(12)	119.76(14)
C(3)—C(2)—N(1)	119.3(2)	O(2)—C(10)—C(11)	123.1(2)	C(8)—C(14)—C(13)	122.5(2)
C(4)—C(3)—C(2)	119.1(2)	O(2)—C(10)—C(9)	119.4(2)	C(8)—C(14)—C(9)	117.2(2)
C(3)—C(4)—C(12)	121.2(2)	C(11)—C(10)—C(9)	117.17(14)	C(13)—C(14)—C(9)	120.1(2)

In the crystal, the molecules are arranged in a staggered fashion. The molecular planes are virtually perpendicular to the *Y* axis and are extended along the *Z* axis.

A comparison of the geometric parameters of nonsubstituted phenanthrene-9,10-quinone, 2,5-dinitrophenanthrene-9,10-quinone, and 2,4,7-trinitrophenanthrene-9,10-quinone demonstrated that the introduction of two or three nitro groups into the phenanthrene nucleus leads to a substantial change in the bond lengths and bond angles in the *ortho*-quinone fragment involved in nucleophilic addition reactions.

The results of this work demonstrate that the ability of C=O groups to add water molecules is determined by both the intramolecular factor (the number of electron-withdrawing substituents in the molecule) and the external factor (the type of the solvent). The results of hydration of tri-, di-, and mononitro derivatives of phenanthrenequinone in the same solvent (for example, in HMPA or DMF) count in favor of the importance of the former factor. The role of the latter factor is confirmed by the results of hydration of the same compound in different solvents.

As demonstrated above, the role of the solvent is determined primarily by its ability to stabilize di(tetra)hydroxydihydrophenanthrenes through intermolecular hydrogen bonding. Actually, the strength of intermolecular hydrogen bonds between the solvent molecule and the OH groups of hydroxydihydrophenanthrenes should correlate with the donor number of the solvent (*DN*), which reflects the ability of the solvent to act as an electron-pair donor in the reaction with acceptor molecules. The values of *DN* for HMPA, DMSO, DMF, and water are 38.8, 29.8, 26.6, and 18, respectively.[9] Consequently, the strength of the intermolecular O—H...O=X hydrogen bond should decrease in this series, which agrees with the above-described experimental results.

It was of interest to elucidate the nature of the effect of the number of nitro groups in the phenanthrenequinone molecule in the case of nucleophilic addition of water.

The ease of addition of water to the carbonyl group should depend on the value of the positive charge on the carbon atom[10] and on the steric accessibility of this atom. In the series of compounds under study, the steric accessibility of the carbonyl groups and the activity of the nucleophilic reagent (water) remain unchanged. The results of our quantum-chemical calculations (PPP) of nonsubstituted phenanthrene-9,10-quinone and compounds **1** and **6**—**9** demonstrated that the positive π charges on the C atoms of the carbonyl groups do not increase as the number of nitro groups increases (contrary to what might be expected) and rather slightly decrease. At the same time, the values of E_{LUMO} noticeably decrease as the number of nitro groups increases. This agrees with our results, because the attack of the nucleophile in the reaction under consideration occurs on LUMO.

Experimental

IR spectra of samples were recorded on Perkin—Elmer 598, Specord M-80, and Bruker IFS-25 spectrophotometers in KCl pellets and in solutions in CCl_4.

Reagent-grade or chemically-pure grade HMPA, DMF, and DMSO were used without additional purification.

Compounds **1** (m.p. 213—214 °C)[11], **6** (m.p. 302—303 °C)[12], **7** (m.p. 228—230 °C)[12], **8** (m.p. 177—179 °C),[13] and **9** (m.p. 256—258 °C)[13] were prepared according to known procedures by nitration of phenanthrene-9,10-quinone (m.p. 208—209 °C). The stretching vibration bands of the C=O and NO_2 groups of these compounds are given in Table 1.

Solvate of 10,10-dihydroxy-2,4,7-trinitro-9,10-dihydrophenanthren-9-one with DMSO (10). A solution of compound **1** (0.5 g) in DMSO (5 mL) was filtered and kept in a closed vessel for 3 weeks. The crystals that formed were filtered off, washed with CCl_4, and dried in air. The solvate (1 : 2) of 10,10-dihydroxy-2,4,7-trinitro-9,10-dihydrophenanthren-9-one with DMSO (**10**) was obtained as pale-orange crystals, m.p. 94—96 °C. Found (%): C, 42.05; H, 3.46;

Table 4. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (U_{eq}) in structure **7**

Atom	x	y	z	$U_{eq} \cdot 10^3/Å^2$
O(1)	4339(2)	4400(2)	−1621(1)	53(1)
O(2)	2957(2)	3706(2)	−3842(2)	54(1)
O(3)	−2185(3)	3619(2)	−6885(1)	77(1)
O(4)	−4547(2)	3853(2)	−6420(2)	57(1)
O(5)	−2720(2)	2407(1)	−1226(1)	47(1)
O(6)	−3139(2)	3433(2)	179(1)	50(1)
N(1)	−3045(2)	3774(2)	−6161(2)	41(1)
N(2)	−2280(2)	3087(1)	−485(1)	34(1)
C(1)	−508(2)	3738(2)	−4608(2)	32(1)
C(2)	−2206(2)	3844(1)	−4902(2)	30(1)
C(3)	−3148(2)	4016(2)	−4057(2)	32(1)
C(4)	−2376(2)	4006(2)	−2874(2)	30(1)
C(5)	−553(2)	3483(1)	−297(2)	30(1)
C(6)	278(2)	3500(2)	879(2)	36(1)
C(7)	1952(3)	3741(2)	1165(2)	38(1)
C(8)	2781(2)	3950(2)	263(2)	36(1)
C(9)	2916(2)	4089(2)	−1836(2)	33(1)
C(10)	2099(2)	3797(2)	−3108(2)	32(1)
C(11)	263(2)	3752(1)	−3410(2)	28(1)
C(12)	−663(2)	3822(1)	−2515(2)	26(1)
C(13)	200(2)	3735(1)	−1249(1)	26(1)
C(14)	1924(2)	3942(1)	−916(2)	29(1)

N, 8.36; O, 34.72; S, 11.98. $C_{14}H_7N_3O_9 \cdot 2C_2H_6OS$. Calculated (%): C, 41.78; H, 3.68; N, 8.12; O, 34.04; S, 12.38. IR (KCl), ν/cm^{-1}: 3550—2600 (OH); 3082 (C_{Ar}—H); 2922, 2852 (CH_3); 1736 (C=O); 1540, 1526 (ν_{as} NO_2); 1350 (ν_s NO_2); 1008 (S=O).

Solvate of 10,10-dihydroxy-2,7-dinitro-9,10-dihydrophenanthren-9-one with HMPA (11). A solution of compound **6** (0.72 g) in HMPA (10 mL) was filtered and kept for 3 months. The white crystalline compound that formed was filtered off and dried in air. The solvate (1 : 2) of 10,10-dihydroxy-2,7-dinitro-9,10-dihydrophenanthren-9-one with HMPA (**11**) was obtained, decomp. point (in a sealed capillary) 72—74 °C. Found (%): C, 45.65; H, 6.60; N, 17.12; P, 9.16. $C_{14}H_8N_2O_7 \cdot 2C_6H_{18}N_3OP$. Calculated (%): C, 46.29; H, 6.53; N, 16.62; P, 9.20. IR (KCl), ν/cm^{-1}: 3600—2700 (OH); 3084 (C_{Ar}—H); 2920, 2888, 2848 (CH_3); 1724 (C=O); 1524 (ν_{as} NO_2); 1348 (ν_s NO_2); 1196 (P=O).

Saturated solutions of compounds **6**—**9** in DMF and a saturated solution of compound **9** in HMPA yielded the initial crystalline compounds. Single crystals of compound **7** isolated from a solution in DMF were used for X-ray diffraction study.

X-ray diffraction analysis. Brown rhombohedral crystals of compound **7** belong to the monoclinic system. The unit cell parameters: a = 8.212(2) Å, b = 12.731(3) Å, c = 11.519(2) Å, β = 102.20(3)°, V = 1177.1(4) Å^3, ρ_{calc} = 1.683 g cm^{-3}, μ = 0.142 mm^{-1}, space group $P2_1/n$, Z = 4. The X-ray diffraction intensity data were collected on an automated four-circle Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, $2\theta_{max}$ = 57°) from a crystal of dimensions 0.36×0.45×0.21 mm. A total of 2403 independent reflections were measured. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method. The positions of the H atoms were calculated geometrically and are included in the refinement on conditions that d(C—H) = 0.96 Å and U_{eq} = 0.02 Å^2. The final R factors for 2347 reflections with $I > 2\sigma(I)$ were as follows: R_1 = 0.059 and wR_2 = 0.15. For all reflections, the R factors were R_1 = 0.062 and wR_2 = 0.17. All calculations were performed on an IBM PC-386 computer using the SHELX 76,[14] SHELXS 86,[15] and SHELXL 93 [16] program packages. The atomic coordinates, interatomic distances, and bond angles for compound **7** are given in Tables 4, 2, and 3, respectively.

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Received April 29, 1998;
in revised form June 30, 1998