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UNEXPECTED FORMATION OF NAPHTHO[2,1-*d*]THIAZOLE-6,9-DIONE FROM 3,5,6-TRICHLORO-2-[2-(*E*-PHENYLDIAZENYL)-THIAZOL-5-YL]-1,4-BENZOQUINONE

N. Batenko,[1]* S. Belyakov,[2] and R. Valters[1]

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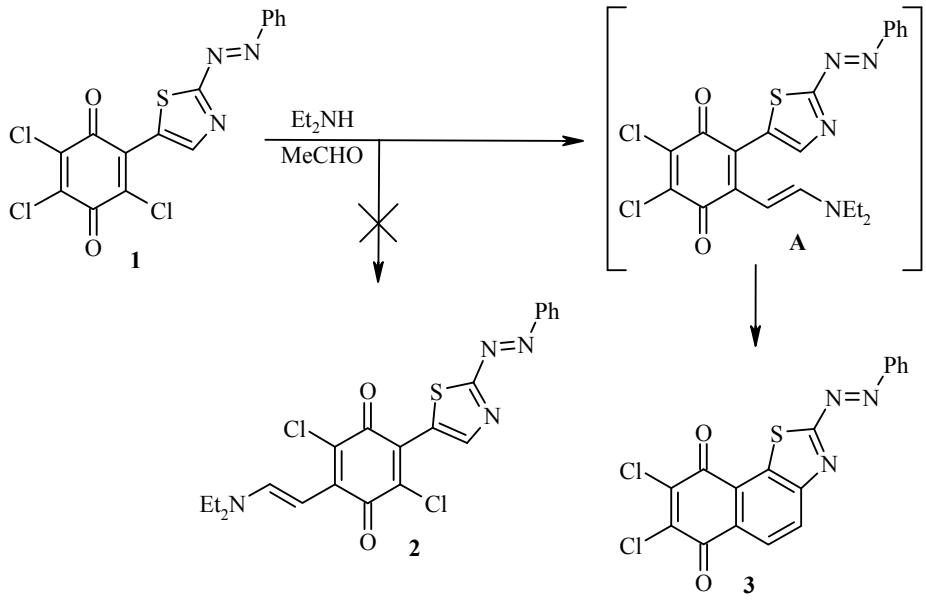
In previous work [1, 2], we showed that the reaction of 2-(2-*N,N*-dialkylaminothiazol-5-yl)-3,5,6-trichloro-1,4-benzoquinones and a *C*-nucleophile, namely, *N,N*-diethyl-*N*-vinyl amine, proceeds with substitution of the chlorine atom at C-5 in the benzoquinone ring, leading to the corresponding diethylaminovinyl derivative. In a continuation of our studies on the synthesis of heterocyclic quinones [1, 2], we carried out a reaction between 3,5,6-trichloro-2-[2-(*E*-phenyldiazenyl)thiazol-5-yl]-1,4-benzoquinone (**1**) [3] and *N,N*-diethyl-*N*-vinylamine, with the latter obtained *in situ* from diethylamine and acetaldehyde. However, we obtained a cyclization product, namely, 7,8-dichloro-2-(*E*-phenyldiazenyl)naphtho[2,1-*d*]thiazole-6,9-dione (**3**) instead of the expected 5-diethyl-aminovinylbenzoquinone **2**.



*To whom correspondence should be addressed, e-mail: nelli.batenko@rtu.lv.

[1]Riga Technical University, 14/24, Azenes St., Riga LV-1048, Latvia.
[2]Latvian Institute of Organic Chemistry, 21 Aizkraukles St., Riga LV-1006, Latvia; e-mail: serg@osi.lv.

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In all likelihood, this reaction proceeds through substitution of the chlorine atom at the C-3 atom of the benzoquinone ring to give intermediate **A**, followed by formation of the aromatic system **3**. The compounds studied in our previous work [1, 2], for which substitution of the chlorine atom at the position C-5 in the benzoquinone ring was observed, had electron-donor dialkylamino groups at the position C-2 in the thiazole ring. The presence of an electron-withdrawing phenyldiazenyl substituent at the position C-2 in the thiazole ring is presumably the major factor shifting the reaction toward the formation of naphthothiazole **3**. The structure of naphthothiazole **3** was confirmed by X-ray diffraction structural analysis (Fig. 1).

The X-ray diffraction structural analysis indicates that the atoms lie in a single plane and conjugation encompasses the entire molecule of naphthothiazole **3**. A strong O···Cl–Csp^2 halogen bond was discovered in this crystal structure. The O(22)···Cl(23) distance is 3.221(3) Å, and the O(22)···Cl(23)–C(7) angle is 165.6(2)°. Centrosymmetric molecular dimers are formed by means of this bond in the crystal. We should note that the other chlorine atom in this molecule, namely, Cl(24), does not participate in any sigma-hole interactions. This accounts for the difference in the lengths of the C–Cl bonds in naphthothiazole **3**. Thus, the C(7)–Cl(23) bond length is 1.706(3) Å, while the C(8)–Cl(24) bond length is 1.733(3) Å. An intermolecular π-π interaction is also observed in this crystal structure. Molecules of naphthothiazole **3** form stacks along the monoclinic axis. The distance between the planes of adjacent molecules in a stack is 3.351 Å. The minimal intermolecular atom-atom contact between C(11) and C(17) in the stack is 3.392(4) Å.

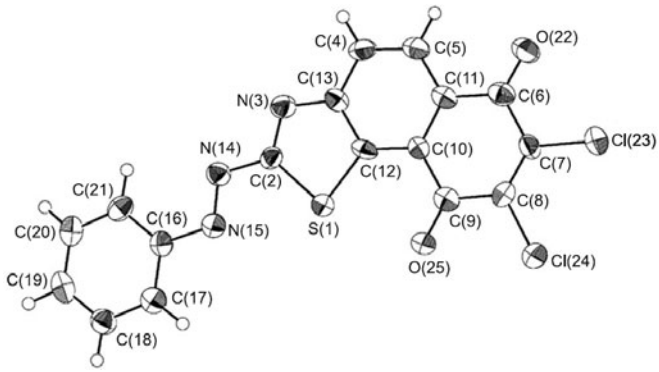

Fig. 1. Molecular structure of naphthothiazole **3** with atoms representated by thermal vibration ellipsoids of 50% probability.

The IR spectrum was recorded on a Thermo Electron Nicolet 5700 spectrometer for KBr pellets. The UV spectrum was recorded on a Perkin Elmer Lambda 35 spectrometer in acetonitrile solution. The ^{1}H NMR spectrum was recorded on a Bruker Avance 300 spectrometer (300 MHz) in $CDCl_3$ with HMDS as internal standard (δ 0.05 ppm). The elemental analysis was carried out on a Carlo Erba EA1108 Elemental Analyzer. The melting points were determined on a Kruss KSP II melting point meter. The course of the reaction and purity of the product were checked by thin-layer chromatography on Merck F254 plates with visualization by UV light.

7,8-Dichloro-2-(*E*-phenyldiazenyl)naphtho[2,1-*d*]thiazole-6,9-dione (3). Acetaldehyde (0.17 ml, 3 mmol) was added to a solution of the trichlorobenzoquinone derivative **1** (0.40 g, 1 mmol) in toluene (30 ml), and then diethylamine (0.21 ml, 2 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 2 h, then evaporated at reduced pressure. The residue was separated on silica gel column with toluene as eluent. Yield 0.14 g (37%). Orange crystals; mp 156-158ºC (toluene). IR spectrum, ν, cm^{-1}: 1503, 1567, 1591, 1663, 1676, 2926. UV spectrum, λ_{max}, nm (log ε): 335 (4.29), 412 (4.14). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.60-7.69 (3H, m, H Ph); 8.15-8.22 (2H, m, H Ph); 8.40 (1H, d, *J* = 8.4, H-5); 8.55 (1H, d, *J* = 8.4, H-4). Found, %: C 52.74; H 1.79; N 10.85. $C_{17}H_7Cl_2N_3O_2S$. Calculated, %: C 52.59; H 1.82; N 10.82.

X-ray Diffraction Structural Investigation of Naphthothiazole 3. Monoclinic monocrystals of

naphthothiazole **3** were obtained by crystallization from toluene. The unit cell parameters of the crystal lattice were as follows: *a* 14.694(2), *b* 6.992(1), *c* 16.664(2) Å, β 111.74(5)°, *V* 1590.3(4); *Z* 4; μ 0.56 mm^{-1}; space group $P2_1/a$. The X-ray diffraction analysis was carried out on a Nonius KappaCCD diffractometer at -100°C using molybdenum radiation (λ = 0.71073 Å). A total of 1998 independent reflections with $I > 3\sigma(I)$ of 3904 measured reflections up to $2\theta_{max}$ 55° were used in the calculations. The structure was solved by the direct method [4] and refined by the full-matrix method of least squares [5]. All the non-hydrogen atoms were refined in anisotropic approximation, and the hydrogen atoms were refined using the "rider" model. The final probability factor was equal to 0.053. The complete data set for this crystal structure has been deposited at the Cambridge Crystallographic Data Center (CCDC deposit 899510).

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