Cycloaddition of C_{60} fullerene to stable 2-RSO_2-benzonitrile oxides

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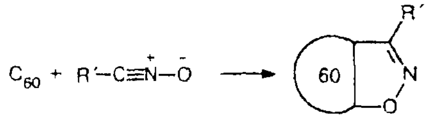
The interaction of stable 2-RSO_2-benzonitrile oxides **1a—c** (R = Ph, Bu^t, or PhMeN) with C_{60} fullerene proceeds at the double (6,6)-bond of fullerene as the [3+2] cycloaddition to form the corresponding isoxazolines **2a—c**. The molecular structure of compound **2b** was established by X-ray structural analysis. The interaction of C_{60} fullerene with 2-(5-methyl-4-nitrothiophene)carbonitrile sulfide, which was obtained by thermolysis of 5-(5′-methyl-4′-nitro-2′-thienyl)-1,3,4-oxathiazol-2-one, affords only unstable products.

Key words: C_{60} fullerene, nitrile oxides, nitrile sulfides, interaction; [3+2] cycloaddition; isoxazolines, crystal structure.

It has been established that fullerenes enter into various cycloaddition reactions, including [3+2] cycloaddition.[1] The interaction of C_{60} fullerene with nitrile oxides, namely, with propio- and acetonitrile oxides obtained *in situ* from the corresponding nitroalkanes, phenyl isocyanate and triethylamine, was first described in 1993.[2] The structures of the monoadducts, which are isoxazoline derivatives formed as a result of [3+2] cycloaddition at the double (6,6)-bond of fullerene, were established based on the analysis of the ^{13}C NMR spectra. Shortly thereafter,[3] the reactions of C_{60} fullerene with stable arenecarbonitrile oxides, such as 9-anthracene- and mesitylenecarbonitrile oxides, and with tosyl- and ethoxycarbonylcarbonitrile oxides, which were obtained *in situ* from the corresponding hydroxymoyl chlorides (*C*-chloroaldoximes), were studied. It was confirmed by X-ray structural analysis that the first of the adducts that was synthesized has an analogous isoxazoline structure. The patent data are available on the addition of nitrile oxides to C_{60} fullerene and on the reduction of the corresponding isoxazoline derivatives to aminoalcohols with lithium aluminum hydride.[4,5] In all cases, the interaction of C_{70} fullerene with nitrile oxides under the conditions described previously[2,3] affords three isomeric isoxazoline monoadducts.[6]

When we started this work, only the interactions of C_{60} fullerene with aceto- and propionitrile oxides were known.[2] We had benzonitrile oxides **1a—c** stabilized by the *o*-RSO_2 groups (R = Ph, Bu^t, or PhMeN)[7,8] at our disposal, and we decided to study their reactivities with respect to C_{60} fullerene and to establish the structures of the adducts that formed.

The interaction of C_{60} fullerene with 1.1 equiv. of nitrile oxide was carried out under an atmosphere of argon in a toluene solution upon heating in a sealed tube (100 °C) for several hours or at room temperature for several days. The reaction mixture was applied to silica gel. After evaporation of toluene, the products were readily separated on silica gel. When benzene was used as the eluent, nonconsumed C_{60} fullerene was eluted almost immediately (~1/3 of the initial amount regardless of the reaction conditions), and then monoadducts were eluted (33—40%). Bisadducts and polyadducts were best eluted with benzene in the presence of acetone.



1a—d **2—d**

R′ = *o*-$PhSO_2C_6H_4$ (**a**), *o*-$Bu^tSO_2C_6H_4$ (**b**), *o*-$PhMeNSO_2C_6H_4$ (**c**), Ph (**d**)

The data of elemental analysis (for S) and the results of mass spectrometry carried out with the use of plasma desorption with ^{252}Cf decay fragments confirmed the monoadduct structures of compounds **2a—c** and the compositions of the corresponding bisadducts **3a—c**.

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The IR spectra of adducts **2a—c** showed intense bands of symmetric (ν_s 1303, 1303, and 1350 cm^{-1}) and asymmetric (ν_{as} 1158, 1148, and 1163 cm^{-1}) stretching vibrations of sulfonyl groups.

The ^{1}H and ^{13}C NMR spectra were recorded only for monoadducts **2a,b**. The low solubility of compound **2c** made it impossible to record its NMR spectrum. For this purpose, the best solvent was tetrachloroethylene. Previously,[9] we have reported the ^{1}H NMR spectrum of adduct **2a** measured in a CS_2—$CDCl_3$ mixture. The ^{1}H NMR spectrum of adduct **2b** showed a singlet of the *tert*-butylsulfonyl group at δ 1.49 and multiplets of four protons of the *o*-phenyl ring at δ 7.7—8.2.

The ^{13}C NMR spectra, which were the most informative, confirmed the isoxazoline structure of monoadducts **2a,b**. The signals of the sp^2-hybridized C atoms of fullerene were observed in the region of δ 136—148. In the spectrum of **2a**, this group consists of two ordinary intensity lines, 22 double intensity lines, and three quadrupole intensity lines (apparently, due to an accidental overlapping of the signals), which is indicative of the C_s symmetry of the adduct that formed (*cf.* Ref. 2). In the case of adduct **2b**, the resolution in this region was somewhat worse. The signal of the sp^2-hybridized C atom of the isoxazoline ring was observed in the spectra of **2a,b** at δ 151.90 and 152.44, respectively. Previously, when the ^{13}C NMR spectrum of compound **2a** was recorded in a CS_2—$CDCl_3$ mixture, we failed to reveal the signals of the sp^3-hybridized C(4) and C(5) atoms because of their low intensities, which did not allow us to exclude the fullerenoid structure of the adduct with one broken C—C bond of the polyhedron.[9] The NMR spectra recorded in tetrachloroethylene in the presence of $Cr(acac)_3$ as the relaxant showed the signals of the C(4) and C(5) atoms (however, of lower intensity) at δ 81.29 and 103.68 for **2a** and at δ 82.03 and 103.30 for **2b**, which, according to the published data,[2,3] provide strong evidence of the isoxazoline structure of the monoadducts. In addition, the NMR spectrum of compound **2a** showed 10 signals of the diphenylsulfonyl fragment of the molecule in the region of δ 127—132. The spectrum of adduct **2b** showed six signals of the *o*-phenylene ring in the region of δ 129—134. The signals of the atoms of the *tert*-butylsulfonyl group were observed at δ 24.67 (3 CH_3) and 61.66 $(-\overset{|}{\underset{|}{C}}-)$.

The results of the X-ray structural analysis of the dark-brown single crystal of **2b** grown from *o*-dichlorobenzene provided the most convincing evidence of the structures of adducts **2a—c** that formed and confirmed the regiochemistry of the cycloaddition of nitrile oxides **1a—c** at the (6,6)-bond of C_{60} fullerene with the formation of the isoxazoline ring.

The overall view of molecule **2b** is shown in Fig. 1. The bond lengths and bond angles in molecule **2b** are given in Tables 1 and 2, respectively. The structure of cycloadduct **2b** is similar to that observed for the analogous isoxazoline adduct **2e**, which was obtained by the

Table 1. Bond lengths (*d*) in molecule **2b**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
C(1)—O(61)	1.468(3)	C(15)—C(16)	1.436(5)	C(32)—C(33)	1.457(5)	C(51)—C(52)	1.390(5)
C(1)—C(9)	1.510(4)	C(15)—C(32)	1.447(5)	C(33)—C(50)	1.387(5)	C(51)—C(60)	1.455(5)
C(1)—C(6)	1.524(4)	C(16)—C(17)	1.380(5)	C(33)—C(34)	1.447(5)	C(52)—C(53)	1.447(5)
C(1)—C(2)	1.580(4)	C(16)—C(34)	1.454(4)	C(34)—C(35)	1.388(5)	C(53)—C(54)	1.398(5)
C(2)—C(63)	1.530(4)	C(17)—C(18)	1.444(5)	C(35)—C(36)	1.442(5)	C(54)—C(55)	1.449(4)
C(2)—C(3)	1.533(4)	C(18)—C(36)	1.394(4)	C(35)—C(52)	1.450(5)	C(55)—C(60)	1.387(4)
C(2)—C(12)	1.533(4)	C(18)—C(19)	1.442(5)	C(36)—C(37)	1.450(5)	C(55)—C(56)	1.448(5)
C(3)—C(4)	1.372(4)	C(19)—C(20)	1.389(5)	C(37)—C(38)	1.385(5)	C(56)—C(57)	1.389(5)
C(3)—C(14)	1.436(4)	C(20)—C(21)	1.432(5)	C(37)—C(53)	1.441(5)	C(57)—C(58)	1.453(5)
C(4)—C(17)	1.452(4)	C(20)—C(38)	1.455(4)	C(38)—C(39)	1.449(5)	C(58)—C(59)	1.395(5)
C(4)—C(5)	1.473(4)	C(21)—C(22)	1.451(5)	C(39)—C(40)	1.394(5)	C(59)—C(60)	1.448(5)
C(5)—C(6)	1.366(4)	C(22)—C(23)	1.372(5)	C(40)—C(54)	1.442(4)	O(61)—N(62)	1.397(3)
C(5)—C(19)	1.445(4)	C(22)—C(39)	1.451(5)	C(40)—C(41)	1.447(5)	N(62)—C(63)	1.279(4)
C(6)—C(7)	1.433(4)	C(23)—C(42)	1.449(5)	C(41)—C(42)	1.391(4)	C(63)—C(64)	1.492(4)
C(7)—C(21)	1.392(4)	C(23)—C(24)	1.466(5)	C(41)—C(56)	1.447(5)	C(64)—C(69)	1.395(4)
C(7)—C(8)	1.443(5)	C(24)—C(25)	1.424(5)	C(42)—C(43)	1.450(5)	C(64)—C(65)	1.404(4)
C(8)—C(24)	1.395(5)	C(25)—C(26)	1.393(5)	C(43)—C(44)	1.374(5)	C(65)—C(66)	1.397(4)
C(8)—C(9)	1.442(4)	C(25)—C(43)	1.455(5)	C(44)—C(57)	1.450(5)	C(65)—S(70)	1.784(3)
C(9)—C(10)	1.363(4)	C(26)—C(27)	1.435(5)	C(44)—C(45)	1.457(5)	C(66)—C(67)	1.385(4)
C(10)—C(26)	1.453(4)	C(27)—C(45)	1.391(5)	C(45)—C(46)	1.442(6)	C(67)—C(68)	1.380(4)
C(10)—C(11)	1.471(4)	C(27)—C(28)	1.453(5)	C(46)—C(47)	1.389(5)	C(68)—C(69)	1.386(4)
C(11)—C(12)	1.376(4)	C(28)—C(29)	1.389(5)	C(46)—C(58)	1.449(4)	S(70)—O(71)	1.439(2)
C(11)—C(28)	1.444(4)	C(29)—C(30)	1.429(5)	C(47)—C(48)	1.446(5)	S(70)—O(72)	1.443(2)
C(12)—C(13)	1.432(4)	C(29)—C(47)	1.459(4)	C(48)—C(49)	1.398(5)	S(70)—C(73)	1.824(3)
C(13)—C(30)	1.399(4)	C(30)—C(31)	1.452(5)	C(49)—C(50)	1.446(5)	C(73)—C(76)	1.519(4)
C(13)—C(14)	1.441(4)	C(31)—C(32)	1.379(5)	C(49)—C(59)	1.450(5)	C(73)—C(75)	1.524(4)
C(14)—C(15)	1.398(4)	C(31)—C(48)	1.452(5)	C(50)—C(51)	1.452(5)	C(73)—C(74)	1.535(4)

Table 2. Bond angles (ω) in molecule **2b**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(61)—C(1)—C(9)	109.8(2)	C(19)—C(20)—C(21)	119.8(3)	C(42)—C(41)—C(40)	119.8(3)
O(61)—C(1)—C(6)	109.8(2)	C(19)—C(20)—C(38)	119.9(3)	C(42)—C(41)—C(56)	119.8(3)
C(9)—C(1)—C(6)	101.6(2)	C(21)—C(20)—C(38)	107.9(3)	C(40)—C(41)—C(56)	108.2(3)
O(61)—C(1)—C(2)	104.5(2)	C(7)—C(21)—C(20)	119.2(3)	C(41)—C(42)—C(23)	119.6(3)
C(9)—C(1)—C(2)	115.7(2)	C(7)—C(21)—C(22)	120.0(3)	C(41)—C(42)—C(43)	119.9(3)
C(6)—C(1)—C(2)	115.4(2)	C(20)—C(21)—C(22)	108.7(3)	C(23)—C(42)—C(43)	108.5(3)
C(63)—C(2)—C(3)	113.5(2)	C(23)—C(22)—C(39)	119.6(3)	C(44)—C(43)—C(42)	120.2(3)
C(63)—C(2)—C(12)	116.0(2)	C(23)—C(22)—C(21)	120.4(3)	C(44)—C(43)—C(25)	120.0(3)
C(3)—C(2)—C(12)	100.1(2)	C(39)—C(22)—C(21)	107.6(3)	C(42)—C(43)—C(25)	107.5(3)
C(63)—C(2)—C(1)	99.2(2)	C(22)—C(23)—C(42)	121.0(3)	C(43)—C(44)—C(57)	120.2(3)
C(3)—C(2)—C(1)	114.4(2)	C(22)—C(23)—C(24)	120.2(3)	C(43)—C(44)—C(45)	120.7(3)
C(12)—C(2)—C(1)	114.5(2)	C(42)—C(23)—C(24)	106.9(3)	C(57)—C(44)—C(45)	107.3(3)
C(4)—C(3)—C(14)	119.3(3)	C(8)—C(24)—C(25)	119.9(3)	C(27)—C(45)—C(46)	120.3(3)
C(4)—C(3)—C(2)	123.4(3)	C(8)—C(24)—C(23)	119.1(3)	C(27)—C(45)—C(44)	119.2(3)
C(14)—C(3)—C(2)	110.2(2)	C(25)—C(24)—C(23)	108.7(3)	C(46)—C(45)—C(44)	108.5(3)
C(3)—C(4)—C(17)	120.4(3)	C(26)—C(25)—C(24)	119.7(3)	C(47)—C(46)—C(45)	120.3(3)
C(3)—C(4)—C(5)	120.8(3)	C(26)—C(25)—C(43)	119.2(3)	C(47)—C(46)—C(58)	120.0(4)
C(17)—C(4)—C(5)	107.1(3)	C(24)—C(25)—C(43)	108.4(3)	C(45)—C(46)—C(58)	108.0(3)
C(6)—C(5)—C(19)	120.2(3)	C(25)—C(26)—C(27)	120.8(3)	C(46)—C(47)—C(48)	120.2(3)
C(6)—C(5)—C(4)	120.4(3)	C(25)—C(26)—C(10)	120.0(3)	C(46)—C(47)—C(29)	119.8(3)
C(19)—C(5)—C(4)	107.7(3)	C(27)—C(26)—C(10)	108.6(3)	C(48)—C(47)—C(29)	107.3(3)
C(5)—C(6)—C(7)	119.6(3)	C(45)—C(27)—C(26)	120.1(3)	C(49)—C(48)—C(47)	120.1(3)
C(5)—C(6)—C(1)	123.8(3)	C(45)—C(27)—C(28)	119.7(3)	C(49)—C(48)—C(31)	119.5(3)
C(7)—C(6)—C(1)	109.6(3)	C(26)—C(27)—C(28)	108.2(3)	C(47)—C(48)—C(31)	108.4(3)
C(21)—C(7)—C(6)	121.0(3)	C(29)—C(28)—C(11)	120.4(3)	C(48)—C(49)—C(50)	119.9(3)
C(21)—C(7)—C(8)	119.8(3)	C(29)—C(28)—C(27)	120.1(3)	C(48)—C(49)—C(59)	119.7(3)
C(6)—C(7)—C(8)	108.3(3)	C(11)—C(28)—C(27)	108.3(3)	C(50)—C(49)—C(59)	108.3(3)
C(24)—C(8)—C(9)	120.2(3)	C(28)—C(29)—C(30)	119.5(3)	C(33)—C(50)—C(49)	120.3(3)
C(24)—C(8)—C(7)	120.5(3)	C(28)—C(29)—C(47)	119.8(3)	C(33)—C(50)—C(51)	119.6(3)
C(9)—C(8)—C(7)	108.5(3)	C(30)—C(29)—C(47)	108.3(3)	C(49)—C(50)—C(51)	107.9(3)
C(10)—C(9)—C(8)	120.0(3)	C(13)—C(30)—C(29)	119.5(3)	C(52)—C(51)—C(50)	120.1(3)
C(10)—C(9)—C(1)	123.3(3)	C(13)—C(30)—C(31)	120.0(3)	C(52)—C(51)—C(60)	119.7(3)
C(8)—C(9)—C(1)	109.5(3)	C(29)—C(30)—C(31)	108.6(3)	C(50)—C(51)—C(60)	107.9(3)
C(9)—C(10)—C(26)	120.0(3)	C(32)—C(31)—C(48)	120.5(3)	C(51)—C(52)—C(35)	119.9(3)
C(9)—C(10)—C(11)	121.5(3)	C(32)—C(31)—C(30)	120.2(3)	C(51)—C(52)—C(53)	120.4(3)
C(26)—C(10)—C(11)	107.3(3)	C(48)—C(31)—C(30)	107.4(3)	C(35)—C(52)—C(53)	108.0(3)
C(12)—C(11)—C(28)	120.4(3)	C(31)—C(32)—C(15)	120.2(3)	C(54)—C(53)—C(37)	120.2(3)
C(12)—C(11)—C(10)	120.1(3)	C(31)—C(32)—C(33)	119.9(3)	C(54)—C(53)—C(52)	119.7(3)
C(28)—C(11)—C(10)	107.6(3)	C(15)—C(32)—C(33)	108.0(3)	C(37)—C(53)—C(52)	108.0(3)
C(11)—C(12)—C(13)	119.0(3)	C(50)—C(33)—C(34)	120.5(3)	C(53)—C(54)—C(40)	119.5(3)
C(11)—C(12)—C(2)	123.2(3)	C(50)—C(33)—C(32)	119.8(3)	C(53)—C(54)—C(55)	119.9(3)
C(13)—C(12)—C(2)	110.3(2)	C(34)—C(33)—C(32)	107.4(3)	C(40)—C(54)—C(55)	108.5(3)
C(30)—C(13)—C(12)	121.2(3)	C(35)—C(34)—C(33)	119.8(3)	C(60)—C(55)—C(56)	120.4(3)
C(30)—C(13)—C(14)	119.5(3)	C(35)—C(34)—C(16)	120.0(3)	C(60)—C(55)—C(54)	120.2(3)
C(12)—C(13)—C(14)	108.6(2)	C(33)—C(34)—C(16)	108.3(3)	C(56)—C(55)—C(54)	107.5(3)
C(15)—C(14)—C(3)	120.6(3)	C(34)—C(35)—C(36)	119.9(3)	C(57)—C(56)—C(55)	119.8(3)
C(15)—C(14)—C(13)	120.4(3)	C(34)—C(35)—C(52)	120.0(3)	C(57)—C(56)—C(41)	120.0(3)
C(3)—C(14)—C(13)	108.4(2)	C(36)—C(35)—C(52)	107.9(3)	C(55)—C(56)—C(41)	108.0(3)
C(14)—C(15)—C(16)	119.2(3)	C(18)—C(36)—C(35)	120.1(3)	C(56)—C(57)—C(44)	119.9(3)
C(14)—C(15)—C(32)	119.7(3)	C(18)—C(36)—C(37)	119.7(3)	C(56)—C(57)—C(58)	120.0(3)
C(16)—C(15)—C(32)	108.5(3)	C(35)—C(36)—C(37)	108.0(3)	C(44)—C(57)—C(58)	108.3(3)
C(17)—C(16)—C(15)	120.1(3)	C(38)—C(37)—C(53)	120.2(3)	C(59)—C(58)—C(46)	120.0(3)
C(17)—C(16)—C(34)	119.8(3)	C(38)—C(37)—C(36)	120.3(3)	C(59)—C(58)—C(57)	120.0(3)
C(15)—C(16)—C(34)	107.9(3)	C(53)—C(37)—C(36)	108.2(3)	C(46)—C(58)—C(57)	107.9(3)
C(16)—C(17)—C(18)	120.4(3)	C(37)—C(38)—C(39)	119.9(3)	C(58)—C(59)—C(60)	119.8(3)
C(16)—C(17)—C(4)	120.1(3)	C(37)—C(38)—C(20)	119.8(3)	C(58)—C(59)—C(49)	120.1(3)
C(18)—C(17)—C(4)	108.4(3)	C(39)—C(38)—C(20)	107.9(3)	C(60)—C(59)—C(49)	108.0(3)
C(36)—C(18)—C(19)	120.1(3)	C(40)—C(39)—C(22)	120.0(3)	C(55)—C(60)—C(59)	120.0(3)
C(36)—C(18)—C(17)	119.8(3)	C(40)—C(39)—C(38)	119.9(3)	C(55)—C(60)—C(51)	120.0(3)
C(19)—C(18)—C(17)	108.4(3)	C(22)—C(39)—C(38)	107.9(3)	C(59)—C(60)—C(51)	107.9(3)
C(20)—C(19)—C(18)	120.2(3)	C(39)—C(40)—C(54)	120.3(3)	N(62)—O(61)—C(1)	110.8(2)
C(20)—C(19)—C(5)	120.0(3)	C(39)—C(40)—C(41)	120.0(3)	C(63)—N(62)—O(61)	110.2(2)
C(18)—C(19)—C(5)	108.3(3)	C(54)—C(40)—C(41)	107.7(3)	N(62)—C(63)—C(64)	118.7(2)

(to be continued)

Table 2. (*continued*)

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N(62)—C(63)—C(2)	115.0(2)	C(67)—C(66)—C(65)	120.4(3)	O(72)—S(70)—C(73)	107.32(14)
C(64)—C(63)—C(2)	125.8(2)	C(68)—C(67)—C(66)	119.5(3)	C(65)—S(70)—C(73)	106.81(13)
C(69)—C(64)—C(65)	118.0(3)	C(67)—C(68)—C(69)	120.6(3)	C(76)—C(73)—C(75)	110.9(3)
C(69)—C(64)—C(63)	117.2(2)	C(68)—C(69)—C(64)	121.1(3)	C(76)—C(73)—C(74)	110.3(3)
C(65)—C(64)—C(63)	124.7(2)	O(71)—S(70)—O(72)	118.26(13)	C(75)—C(73)—C(74)	110.7(3)
C(66)—C(65)—C(64)	120.4(3)	O(71)—S(70)—C(65)	108.42(13)	C(76)—C(73)—S(70)	109.8(2)
C(66)—C(65)—S(70)	115.7(2)	O(72)—S(70)—C(65)	106.25(13)	C(75)—C(73)—S(70)	110.0(2)
C(64)—C(65)—S(70)	123.8(2)	O(71)—S(70)—C(73)	109.21(13)	C(74)—C(73)—S(70)	104.9(2)

reaction of C_{60} fullerene with 9-anthracenecarbonitrile oxide.[3] As in the case of adduct **2e**, the fullerene nucleus of **2b** undergoes substantial deformations upon cycloaddition. Thus, all five-membered and six-membered rings of the fullerene fragment, except for four rings involving the C(1) and C(2) atoms, are planar to within 0.01 Å, whereas the five-membered C(1)C(6)C(7)C(8)C(9) and C(2)C(3)C(14)C(13)C(12) rings adopt a flattened envelope conformation. The deviations of the C(1) and C(2) atoms from the mean planes through the other four atoms of the corresponding cycles are identical (0.254 Å). Two six-membered C(1)C(2)C(3)C(4)C(5)C(6) and C(1)C(2)C(12)C(11)C(10)C(9) rings are also substantially nonplanar, and have a flattened boat conformation: the C(3) and C(6) atoms deviate from the C(1)C(2)C(4)C(5) plane by 0.127 and 0.099 Å, respectively, and the C(9) and C(12) atoms deviate from the C(1)C(2)C(10)C(11) plane by 0.097 and 0.120 Å, respectively.

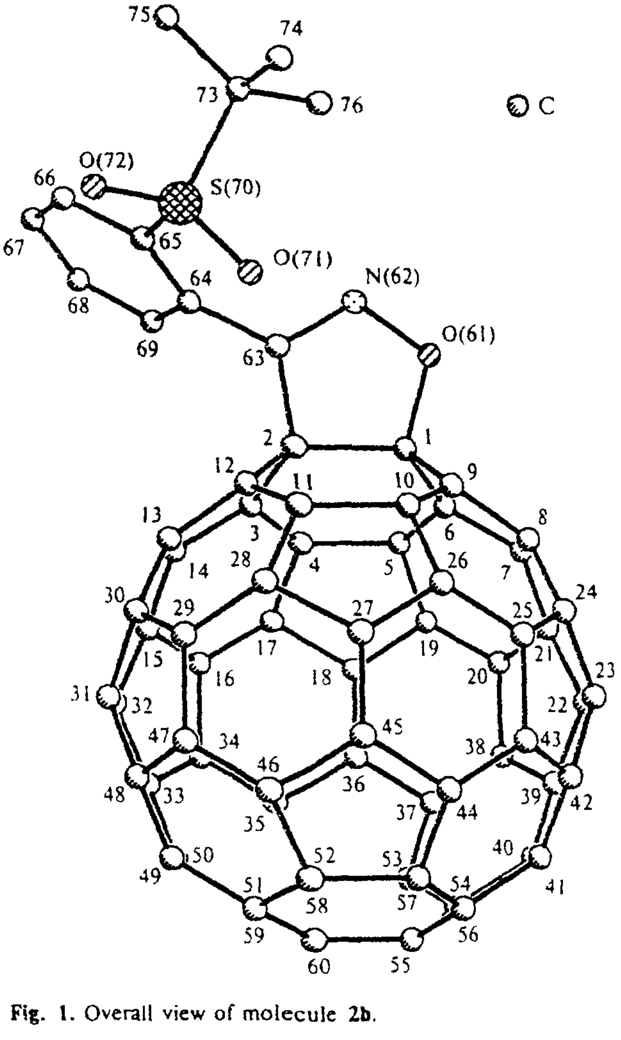


Fig. 1. Overall view of molecule **2b**.

It is convenient to estimate the deformation of the fullerene nucleus by the distance between the center of this fragment and the carbon atoms (the C(1) and C(2) atoms and the opposing C(55) and C(60) atoms were omitted from the calculations of the coordinates of the center of the fragment). The average value of this distance for molecule **2b** (3.533 Å) agrees with the data from the recent work,[10] which presented the results of the statistical analysis of the geometry of all derivatives of C_{60} fullerene available in the Cambridge Structural Database (CSD). In molecule **2b**, the distances between the center of the fullerene nucleus and the C(1) and C(2) atoms increase to 3.825 and 3.862 Å, respectively. The small difference in these distances is, apparently, due to the different nature of substituents at the C(1) and C(2) atoms (the O and C atoms, respectively). Unfortunately, the analogous data on the geometry of the fullerene fragment of isoxazoline adduct **2e** were not reported,[3] and these parameters cannot be calculated because the atomic coordinates for this structure are absent in the CSD. An alternative way of describing the distortions of the fullerene nucleus used in Ref. 3 consists in calculations of different "diameters" of the C_{60} skeleton. Thus, in molecule **2b**, the distance between the midpoints of the C(1)—C(2) and C(55)—C(60) bonds is 7.236 Å (in **2e**, the corresponding value is 7.231 Å). The perpendicular "diameters" calculated as the distances between the midpoints of the C(22)—C(23), C(31)—C(32) and C(18)—C(36), C(27)—C(45) bonds are 6.944 and 6.893 Å, respectively (see Ref. 3: only one, apparently, average value (6.906 Å) was given). In molecule **2b**, the three "diameters" (which are, apparently, in different orientations with respect to the C(1)—C(2) bond) of the fullerene nucleus are substantially different. This difference was observed by X-ray structural analysis in both monometal $(\eta^2\text{-}C_{60})ML_n$ complexes[10] and fullerene derivatives with σ-substituents at the adjacent C atoms (see, for example, the structure of 1,2-dihydro-64,65-dimethoxy-1,2-(methano[1,2]benzomethano)-[60]fullerene,[11] in which the fullerene nucleus is fused to the six-membered carbocycle at the C—C bond).

The average values of the 5,6- and 6,6-bonds in molecule **2b** (except for the bonds involving the C(1) and C(2) atoms) are 1.447 and 1.387 Å, respectively, which agree with the "classical" structural formula of the fullerene nucleus with single bonds for 5,6-edges and double bonds for 6,6-edges and with the data on the values averaged over the fullerene structures available in the CSD (1.450 and 1.390 Å, respectively).[10] The single C(1)—C(2) bond, which forms as a result of cycloaddition, is substantially elongated (1.580(4) Å and 1.584 Å in molecules **2b** and **2e**, respectively) even compared to the standard value for the $C(sp^3)-C(sp^3)$ bond (1.530 Å),[12] which is attributable to an eclipsed arrangement of all substituents (the average torsion angle is 1.8°).

The bond lengths in the fused heterocycle and in the *o-tert*-butylsulfonylphenyl substituent are close to the table values.[12] The five-membered heterocycle adopts a substantially flattened envelope conformation: the N(62) atom deviates from the mean plane through the remaining four atoms of the ring toward the *tert*-butylsulfonyl group by 0.068 Å. The O(61)C(1)C(2)C(63) plane is nearly in the mirror symmetry plane of the fullerene fragment. The dihedral angle between this plane and the planes of the fused six-membered rings are 120.8° and 122.6°. The phenyl substituent at the C(63) atom is rotated by 76.1° relative to the plane of the five-membered heterocycle (the anthracene substituent in adduct **2e** is virtually perpendicular to the plane of the heterocycle (87.7°)). The C(64)—C(65)—S(70)—C(73) torsion angle is 101.7°.

Based on the analysis of the abundant structural data reported in the recent review,[13] the minimum values of the different types of shortened van der Waals contacts were obtained (C...C, 3.27 Å; C...Cl, 3.45 Å; and Cl...Cl, 3.65 Å). Based on these values, five contacts between the C atoms of the adjacent fullerene fragments, four contacts between the Cl atoms of solvate *o*-dichlorobenzene molecules and the C atoms of the adjacent fullerene fragments, and the Cl...Cl and Cl...C contacts between the neighboring *o*-dichlorobenzene molecules (Table 3) can be found in the crystal structure of **2b** · $2C_6H_4Cl_2$. According to the published data,[13] these contacts correspond to specific interactions.

However, it should be remembered that intermolecular contacts in fullerene structures, apparently, call for an additional analysis, and the above-mentioned general data[13] should be applied to these structures with caution.

The crystal packing of solvate **2b** · $2C_6H_4Cl_2$ shows several more interesting features. The closest coordination sphere about each C_{60} fragment contains four analogous fragments located at the vertices of the distorted tetrahedron at distances of 10.830, 9.890, 9.932, and 9.932 Å (these distances are calculated as the distances between the centers of the corresponding C_{60} fragments). For comparison, the distance between the fullerene nuclei in the face-centered cubic structure of the unsubstituted C_{60} fullerene is 9.943 Å (calculated based on the published data[14] for the low-temperature experiment). Therefore, the packing of fullerene nuclei in the crystal of **2b** · $2C_6H_4Cl_2$ is, clearly, looser than that of the unsubstituted fullerene and is based on the motif of the diamond structure (in the crystal of **2b** · $2C_6H_4Cl_2$, the centers of fullerene atoms are considered in place of the C atoms of the diamond structure). An analogous packing of C_{60} fragments was observed[15] in the structure of crystal solvate $(\eta^2\text{-}C_{60})Pt(DIOP) \cdot C_8H_{14}$ with the shortest distances between the fullerene nuclei of 10.103 and 10.295 Å. Figure 2 shows the fragment of the crystal packing of **2b** · $2C_6H_4Cl_2$ projected along the *y* axis of the crystal. In this figure, the layers of fullerene fragments perpendicular to the plane of the paper and parallel to the (011) plane of the crystal are easily seen. It is remarkable that each layer is located at different distances from the adjacent (the upper and lower) layers, so that the interlayer distances alternate (8.339 and 9.284 Å). This difference in the interlayer distances is caused by the fact that organic substituents are located in the space between closely spaced layers (in Fig. 2, these substituents are represented by small spheres linked to the centers of the corresponding C_{60} fragments), whereas solvate *o*-dichlorobenzene molecules (in Fig. 2, these molecules are represented by isolated spheres) are located between the more remote layers. Apparently, the alternation of the interlayer distances is associated with the substantial elongation of one of the distances in the

Table 3. Shortened intermolecular contacts (*r*) in the crystal structure of **2b** · $2C_6H_4Cl_2$

Contact A...B	Symmetry transformation of the B atom	*r*/Å
C(10)...C(26)	$-1-x,\ 1-y,\ -z$	3.182
C(26)...C(26)	$-1-x,\ 1-y,\ -z$	3.020
C(20)...C(30)	$x,\ 1.5-y,\ 0.5+z$	3.236
C(30)...C(38)	$x,\ 1.5-y,\ -0.5+z$	3.178
C(31)...C(38)	$x,\ 1.5-y,\ -0.5+z$	3.172
Cl(2)...C(57)	$-x,\ 1-y,\ -z$	3.482
Cl(4)...C(52)	$x,\ y,\ z$	3.367
Cl(4′)...C(46)	$-x,\ 1-y,\ -z$	3.386
Cl(4′)...C(58)	$-x,\ 1-y,\ -z$	3.482
Cl(1)...Cl(1)	$-x,\ 2-y,\ -z$	3.196
Cl(2)...Cl(3)	$x,\ 1.5-y,\ -0.5+z$	3.357
Cl(4)...C(77)	$x,\ y,\ z$	3.152
Cl(4)...C(78)	$x,\ y,\ z$	3.426
Cl(4)...C(82)	$x,\ y,\ z$	3.299

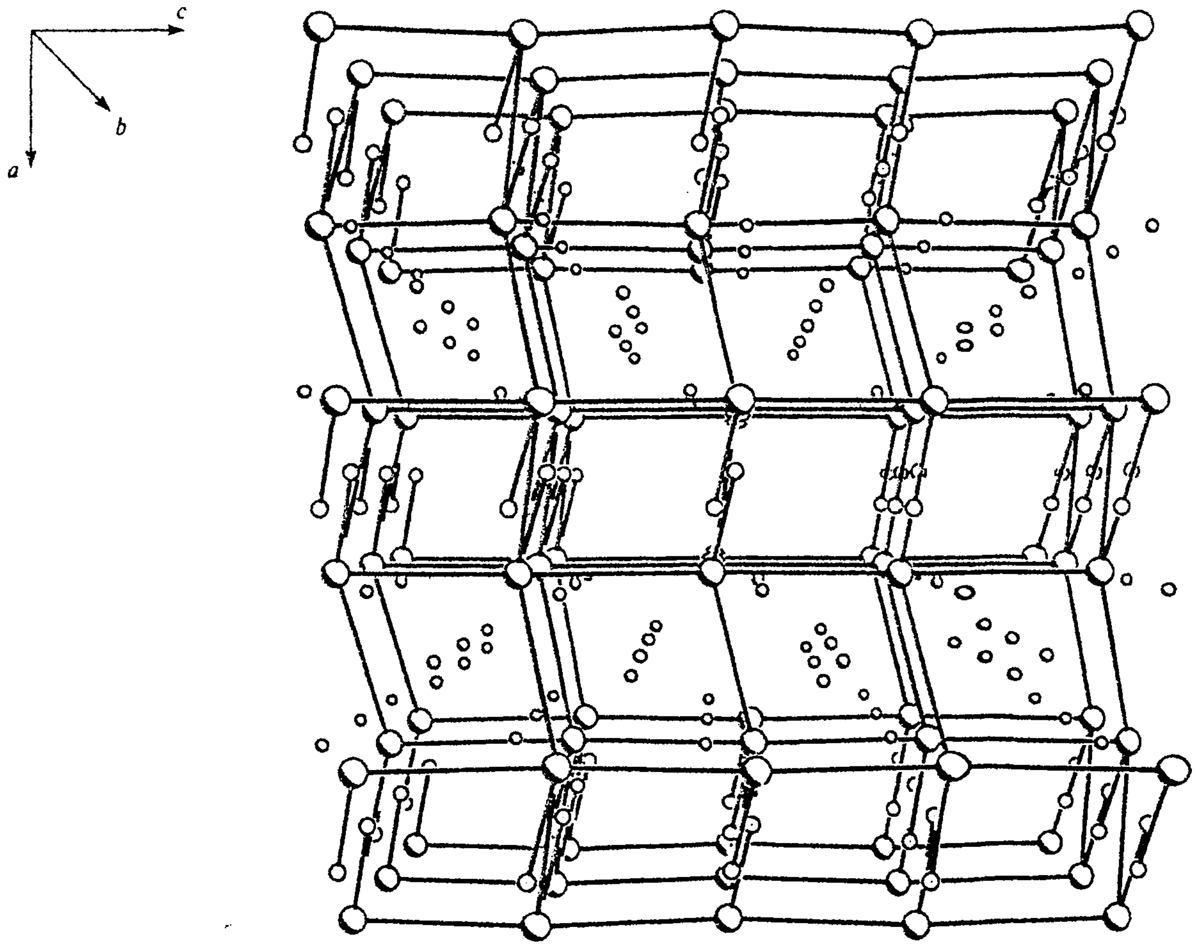
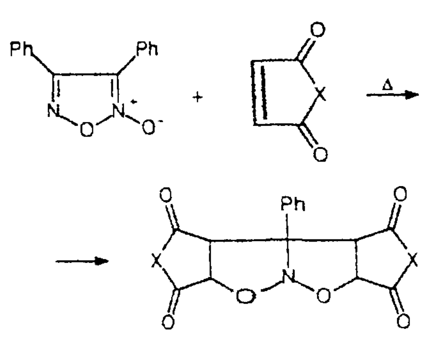


Fig. 2. Crystal packing of **2b** · $2C_6H_4Cl_2$ (the projection along the *y* axis). Centers of fullerene nuclei are represented by large spheres, and the S atoms of the isoxazoline fragment of the molecule (bonded to the corresponding C_{60} nucleus) and centers of solvate *o*-dichlorobenzene molecules are represented by small spheres.

"coordination tetrahedron" about each of the fullerene nuclei (see above).

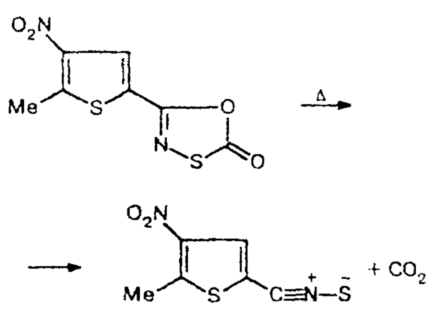
It should be noted that of the five shortened contacts between C atoms of the adjacent fullerene nuclei (see Table 3), three contacts belong to the C_{60} fragments located in a single layer, and two contacts (3.182 and 3.020 Å) belong to the fragments from the adjacent closely spaced layers. One contact (3.020 Å) is substantially shorter than the contacts in the structure of the unsubstituted fullerene (3.128—3.592 Å).[14]

It is known that one source of unstable nitrile oxides is their dimers, heterocyclic furoxans, which form products of [3+2] cycloaddition of nitrile oxides with the corresponding cycloaddition reagents upon thermolysis.[16] However, a new interesting scheme of the thermal interaction, in particular, of 3,4-diphenylfuroxan with maleic anhydride and its amides, was described in 1992 (see Ref. 17).



Studies of the thermal reaction of 3,4-diphenylfuroxan with C_{60} fullerene demonstrated that this reaction proceeded at an appreciable rate only at 190 °C in *o*-dichlorobenzene. In this case, the [3+2] isoxazoline adduct of benzonitrile oxide **1d** with fullerene (**2d**) formed in a yield of 9%. We also obtained this adduct when nitrile oxide **1d** was generated from benzohydroxymoyl chloride with triethylamine in the presence of C_{60} fullerene. The structure of adduct **2d** was unambiguously established by mass spectrometry and ^1H and ^{13}C NMR spectroscopy.

We also studied the possibility of the interaction of nitrile sulfides with C_{60} fullerene. For this purpose, we synthesized 5-(5′-methyl-4′-nitro-2′-thienyl)-1,3,4-oxathiazol-2-one, the precursor of 2-(5-methyl-4-nitrothiophene)carbonitrile sulfide. With the aim of finding the optimum conditions for cycloaddition, we obtained the derivatogram of the thermal decomposition of oxathiazolone. It was found that the decomposition of this compound with elimination of CO_2 proceeded most vigorously at 185 °C.



Because of this, the cycloaddition of C_{60} fullerene to nitrile sulfide that formed upon thermal decomposition was carried out in a solution of boiling *o*-dichlorobenzene under a stream of argon followed by separation of the reaction mixture on silica gel. First, nonconsumed fullerene and then the brown zone of the expected adduct were eluted with benzene. However, when we attempted to evaporate or even to store the solution obtained after chromatography, the adduct slowly decomposed to form the initial C_{60} fullerene.

Experimental

The IR spectra of the compounds synthesized were recorded on a Specord 80 instrument using KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer (399.95 and 100.58 MHz, respectively) in a C_2Cl_4—$CDCl_3$ mixture ($Cr(acac)_3$ as the relaxing reagent). The mass spectra were measured on an MCBKh instrument (SELMI, Sumy, Ukraine) by the TOF-PDMS method with ionization with ^{252}Cf decay fragments. Thermal decomposition of 5-(5′-methyl-4′-nitro-2′-thienyl)-1,3,4-oxathiazol-2-one was studied on a Q-1500D derivatograph in the temperature range from 20 to 1000 °C in air with a rate of the increase in the temperature of 10 °C min^{-1}. Calcinated Al_2O_3 was used as the standard.

The syntheses of compounds **1a**,**b**[7] and **1c**[8] were reported previously.

Interaction of C_{60} fullerene with stable 2-RSO_2-benzonitrile oxides (general procedure). A solution of a mixture of C_{60} fullerene (0.08 mmol) and the corresponding nitrile oxide **1a—c** (0.09 mmol) in toluene (60 mL) was heated in a tube under an atmosphere of argon at 110 °C for 8 h (or kept at room temperature for 3 days). The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel. First nonconsumed C_{60} fullerene and then monoadduct **2a—c** were eluted with benzene. Bisadduct **3a—c** was eluted with a benzene—acetone mixture (20 : 1).

3-[*o*-(Phenylsulfonyl)phenyl]-[60]fullereno[1′,2′:4,5]isoxazoline (2a). The yield was 33%. Found (%): S, 2.90. $C_{73}H_9NO_3S$. Calculated (%): S, 3.27. IR, ν/cm^{-1}: 1430, 1303, 1280, 1254, 1178, 1158, 1094, 1015, 856, 780, 743, 670, 575, 530. ^{13}C NMR, δ: 81.29 (C(4), isoxazoline); 103.68 (C(5), isoxazoline); 127.35, 127.98, 128.72, 128.91, 130.47, 130.83, 131.64, 132.56, 132.95, 133.00 (2-$C_6H_5SO_2C_6H_4$); 137.32 (2), 137.63 (2), 140.11 (2), 140.41 (2), 141.68 (2), 142.23 (2), 142.31 (4), 142.37 (2), 142.45 (2), 142.72 (2), 142.78 (2), 142.97 (2), 143.35 (2), 144.14 (2), 144.30 (2), 144.38 (2), 144.58 (2), 144.93 (2), 145.18 (4), 145.33 (2), 145.48 (2), 145.60 (2), 145.87 (2), 145.96 (2), 146.28 (4), 147.27 (1), 147.87 (1) (C_{58}); 151.90 (C(3), isoxazoline). MS, *m/z*: 980 $[M+H]^+$.

Bisadduct 3a. The yield was 22%. Found (%): S, 4.98. $C_{86}H_{18}N_2O_6S_2$. Calculated (%): S, 5.17.

3-[*o*-(*tert*-Butylsulfonyl)phenyl]-[60]fullereno[1′,2′:4,5]isoxazoline (2b). The yield was 40%. Found (%): S, 3.52. $C_{71}H_{13}NO_3S$. Calculated (%): S, 3.34. IR, ν/cm^{-1}: 1429, 1303, 1180, 1148, 1118, 1074, 1070, 980, 858, 780, 766, 744, 670, 574, 529. ^1H NMR, δ: 1.57 (s, 9 H, CMe_3); 7.77 (td, 1 H, H(5), *o*-C_6H_4, *J* = 7.5 Hz, *J* = 1.5 Hz); 7.82 (td, 1 H, H(4), *o*-C_6H_4, *J* = 7.5 Hz, *J* = 1.5 Hz); 7.92 (dd, 1 H, H(6), *o*-C_6H_4, *J* = 7.5 Hz, *J* = 1.5 Hz); 8.14 (dd, 1 H, H(3), *o*-C_6H_4, *J* = 7.5 Hz, *J* = 1.5 Hz). ^{13}C NMR, δ: 24.67 (3 CH_3); 61.66 ($\underline{C}Me_3$); 82.03 (C(4), isoxazoline); 103.30 (C(5), isoxazoline); 129.22, 129.94, 130.15, 132.49, 132.65, 133.82 (*o*-C_6H_4); 137.32 (2), 137.85 (2), 140.07 (2), 140.32 (2), 141.66 (2), 142.26 (2), 142.36 (4), 142.47 (2), 142.71 (2), 142.77 (2), 142.98 (2), 144.19 (2), 144.41 (2), 145.07 (2), 145.19 (8), 145.53 (2), 145.57 (2), 145.87 (2), 145.97 (2), 146.26 (2), 146.29 (8), 147.30 (1), 147.92 (1) (C_{58}); 152.44 (C(3), isoxazoline). MS, *m/z*: 959 $[M]^+$.

Bisadduct 3b. The yield was 20%. MS, *m/z*: 1198 $[M]^+$.

3-[*o*-(*N*-Methyl-*N*-phenylsulfamoyl)phenyl]-[60]fullereno[1′,2′:4,5]isoxazoline (2c). The yield was 37%. Found (%): S, 3.33. $C_{74}H_{12}N_2O_3S$. Calculated (%): S, 3.18. IR, ν/cm^{-1}: 1426, 1350, 1276, 1186, 1163, 1120, 984, 876, 780, 760, 680, 573, 525. MS, *m/z*: 1009 $[M]^+$.

Bisadduct 3c. The yield was 24%. Found (%): S, 5.00. $C_{88}H_{24}N_4O_6S_2$. Calculated (%): S, 4.94. MS, *m/z*: 1297 $[M]^+$.

3-Phenyl-[60]fullereno[1′,2′:4,5]isoxazoline (2d). *A*. A mixture of C_{60} fullerene (0.144 g, 0.2 mmol) and 3,4-diphenylfuroxan (0.024 g, 0.1 mmol) in *o*-dichlorobenzene (15 mL) was heated in a tube under an atmosphere of argon at 195 °C for 41 h. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel. First nonconsumed C_{60} fullerene and then the reaction product **2d** were eluted with a benzene—hexane mixture (1 : 1). The yield of **2d** was 0.015 g (9.2% when calculated for furoxan)

B. A solution of triethylamine (0.016 g, 0.15 mmol) in toluene (10 mL) was added portionwise with stirring to a solution of C_{60} fullerene (0.072 g, 0.1 mmol) and benzohydroxymoyl chloride (0.024 g, 0.15 mmol) in toluene (120 mL) for 4 h. The reaction mixture was kept for 12 h, and the reaction product was isolated as described in method *A*. The yield of compound **2d** was 0.021 g (25%). IR, ν/cm^{-1}: 1428, 1296, 1180, 980, 864, 780, 760, 748, 684, 672, 652, 575,

Table 4. Atomic coordinates (×10^4) and equivalent isotropic temperature factors (U_{eq}×10^3) in the crystal structure of **2b** · $2C_6H_4Cl_2$

Atom	x	y	z	U_{eq}/Å^2
C(1)	−4607(2)	7829(2)	305(2)	21(1)
C(2)	−4277(2)	8139(2)	−403(1)	16(1)
C(3)	−3534(2)	8679(2)	−327(1)	18(1)
C(4)	−3251(2)	9024(2)	290(2)	22(1)
C(5)	−3572(2)	8748(2)	948(2)	24(1)
C(6)	−4158(2)	8141(2)	953(1)	24(1)
C(7)	−4148(2)	7430(2)	1460(2)	28(1)
C(8)	−4446(2)	6613(2)	1135(2)	29(1)
C(9)	−4646(2)	6814(2)	421(2)	23(1)
C(10)	−4509(2)	6189(2)	−79(2)	25(1)
C(11)	−4191(2)	6458(2)	−738(2)	24(1)
C(12)	−4023(2)	7356(2)	−863(1)	19(1)
C(13)	−3319(2)	7376(2)	−1162(1)	21(1)
C(14)	−3018(2)	8387(2)	−835(1)	22(1)
C(15)	−2235(2)	8498(2)	−724(2)	28(1)
C(16)	−1946(2)	8874(2)	−81(2)	30(1)
C(17)	−2438(2)	9124(2)	419(2)	28(1)
C(18)	−2260(2)	8922(2)	1138(2)	30(1)
C(19)	−2955(2)	8689(2)	1462(2)	29(1)
C(20)	−2956(2)	8014(2)	1965(2)	31(1)
C(21)	−3563(2)	7368(3)	1965(2)	31(1)
C(22)	−3255(2)	6485(3)	2162(2)	33(1)
C(23)	−3534(2)	5708(2)	1851(2)	33(1)
C(24)	−4152(2)	5762(2)	1321(2)	34(1)
C(25)	−4024(2)	5100(2)	802(2)	34(1)
C(26)	−4187(2)	5309(2)	110(2)	32(1)
C(27)	−3685(2)	5034(2)	−415(2)	34(1)
C(28)	−3679(2)	5746(2)	−935(2)	29(1)
C(29)	−3010(2)	5961(2)	−1251(2)	31(1)
C(30)	−2822(2)	6894(2)	−1364(1)	28(1)
C(31)	−2009(2)	7007(3)	−1243(2)	32(1)
C(32)	−1725(2)	7787(3)	−931(2)	31(1)
C(33)	−1106(2)	7725(3)	−409(2)	34(1)
C(34)	−1246(2)	8398(2)	116(2)	34(1)
C(35)	−1073(2)	8202(2)	806(2)	33(1)
C(36)	−1588(2)	8471(2)	1327(2)	32(1)
C(37)	−1591(2)	7759(2)	1846(2)	31(1)
C(38)	−2256(2)	7538(2)	2161(2)	31(1)
C(39)	−2442(2)	6593(2)	2283(2)	31(1)
C(40)	−1950(2)	5908(2)	2084(2)	27(1)
C(41)	−2249(2)	5090(2)	1757(2)	29(1)
C(42)	−3029(2)	4991(2)	1641(2)	32(1)
C(43)	−3327(2)	4614(2)	992(2)	36(1)
C(44)	−2843(2)	4358(2)	491(2)	35(1)
C(45)	−3019(2)	4568(2)	−234(2)	36(1)
C(46)	−2322(2)	4794(2)	−557(2)	37(1)
C(47)	−2313(2)	5471(2)	−1058(2)	34(1)
C(48)	−1698(2)	6122(3)	−1054(2)	35(1)
C(49)	−1104(2)	6064(3)	−553(2)	35(1)
C(50)	−806(2)	6882(3)	−228(2)	33(1)
C(51)	−625(2)	6677(2)	495(2)	31(1)
C(52)	−759(2)	7321(2)	1001(2)	30(1)
C(53)	−1079(2)	7052(2)	1645(2)	29(1)
C(54)	−1255(2)	6138(2)	1758(2)	26(1)
C(55)	−1122(2)	5467(2)	1229(2)	27(1)
C(56)	−1740(2)	4818(2)	1230(2)	29(1)
C(57)	−2030(2)	4459(2)	609(2)	33(1)
C(58)	−1707(2)	4728(2)	−38(2)	34(1)
C(59)	−1110(2)	5351(2)	−36(2)	32(1)
C(60)	−814(2)	5727(2)	612(2)	29(1)
O(61)	−5374(1)	8218(2)	294(1)	27(1)
N(62)	−5506(1)	8762(2)	−291(1)	24(1)
C(63)	−4948(2)	8703(2)	−689(1)	19(1)
C(64)	−4964(2)	9259(2)	−1334(1)	19(1)
C(65)	−5391(2)	9047(2)	−1942(1)	18(1)
C(66)	−5398(2)	9636(2)	−2508(2)	20(1)
C(67)	−5000(2)	10448(2)	−2470(2)	23(1)
C(68)	−4583(2)	10663(2)	−1873(2)	25(1)
C(69)	−4550(2)	10069(2)	−1317(2)	23(1)
S(70)	−5933(1)	8029(1)	−2058(1)	20(1)
O(71)	−5691(1)	7391(1)	−1530(1)	27(1)
O(72)	−5869(1)	7768(2)	−2772(1)	29(1)
C(73)	−6922(2)	8334(2)	−1943(2)	22(1)
C(74)	−7359(2)	7433(2)	−2009(2)	31(1)
C(75)	−7193(2)	8998(3)	−2507(2)	35(1)
C(76)	−7005(2)	8743(2)	−1230(2)	30(1)
Cl(1)	606(1)	9367(1)	406(1)	39(1)
Cl(2)	1281(1)	7710(1)	−388(1)	41(1)
C(77)	1501(2)	8956(2)	636(2)	24(1)
C(78)	1798(2)	8228(2)	281(2)	25(1)
C(79)	2513(2)	7903(2)	472(2)	31(1)
C(80)	2925(2)	8299(2)	1012(2)	32(1)
C(81)	2624(2)	9022(2)	1365(2)	29(1)
C(82)	1911(2)	9350(2)	1183(2)	27(1)
Cl(3)*	216(1)	7868(1)	3200(1)	45(1)
Cl(3′)**	651(2)	8198(3)	2376(2)	48(1)
Cl(4)*	973(1)	7593(1)	1776(1)	43(1)
Cl(4′)**	1175(2)	6621(3)	1414(2)	49(1)
C(83)*	360(2)	6786(3)	2872(2)	25(1)
C(83′)**	498(11)	7047(13)	2569(12)	35(4)
C(84)*	683(3)	6675(5)	2243(3)	25(1)
C(84′)**	722(15)	6374(19)	2158(15)	27(6)
C(85)*	774(2)	5803(4)	1982(2)	32(1)
C(85′)*	599(14)	5443(18)	2297(13)	34(5)
C(86)*	548(3)	5052(5)	2360(3)	39(1)
C(86′)**	232(18)	5139(27)	2985(16)	5(6)
C(87)*	225(9)	5211(10)	2978(8)	54(4)
C(87′)**	12(31)	6041(41)	3365(32)	31(11)
C(88)*	135(7)	6035(9)	3244(6)	39(3)
C(88′)*	127(12)	6858(14)	3169(12)	44(4)
H(66)	−5667(17)	9446(21)	−2940(16)	20(8)
H(67)	−5028(20)	10839(25)	−2854(19)	37(10)
H(68)	−4338(18)	11215(23)	−1835(16)	22(8)
H(69)	−4206(18)	10223(22)	−923(17)	26(9)
H(74A)	−7916(24)	7560(27)	−1939(20)	50(11)
H(74B)	−7171(20)	7014(25)	−1655(18)	31(9)
H(74C)	−7313(23)	7181(28)	−2465(23)	49(12)
H(75A)	−7728(26)	9090(28)	−2476(21)	53(12)
H(75B)	−6936(24)	9602(31)	−2467(21)	55(12)
H(75C)	−7109(23)	8734(29)	−2939(23)	45(12)
H(76A)	−6851(25)	8281(31)	−877(23)	60(13)
H(76B)	−7552(24)	8914(23)	−1174(17)	28(9)
H(76C)	−6708(19)	9314(24)	−1167(17)	27(9)
H(79)	2716(21)	7421(27)	251(19)	40(10)
H(81)	2907(20)	9313(24)	1744(19)	35(10)
H(82)	1685(19)	9854(24)	1432(17)	29(9)
H(85)	991(25)	5769(30)	1482(24)	31(12)
H(86)	644(27)	4423(36)	2180(25)	42(14)
H(87)	87(25)	4691(33)	3214(24)	29(12)
H(88)	−120(27)	6069(33)	3692(26)	36(15)

* The occupancy of the position G = 0.8. ** The occupancy of the position G = 0.2.

528. ^{1}H NMR, δ: 7.44 (m, 3 H, Ph); 8.14 (m, 2 H, Ph). ^{13}C NMR, δ: 79.61 (C(4), isoxazoline); 104.52 (C(5), isoxazoline); 128.96, 129.02, 129.47, 130.47 (Ph); 136.76 (2), 137.12 (2), 140.38 (2), 141.77 (2), 142.21 (2), 142.36 (2), 142.43 (2), 142.55 (4), 142.93 (4), 143.07 (2), 143.18 (2), 144.18 (2), 144.52 (2), 144.86 (2), 144.98 (2), 145.05 (2), 145.26 (2), 145.34 (2), 145.52 (2), 145.68 (2), 145.98 (2), 146.04 (2), 146.09 (2), 146.31 (2), 146.36 (2), 146.49 (2), 147.39 (1), 147.89 (1) (C_{58}); 151.35 (C(3), isoxazoline). MS, *m/z* 840 $[M+H]^+$.

5-(5′-Methyl-4′-nitro-2′-thienyl)-1,3,4-oxathiazol-2-one. A solution of the amide of 5-methyl-4-nitro-2-thiophenecarboxylic acid (m.p. 224–225 °C, 0.93 g, 5 mmol) and chlorocarbonylsulfenyl chloride (0.85 mL, 10 mmol) in toluene (20 mL) was refluxed for 20 h. Then the solution was concentrated and crystallized from alcohol. The yield was 0.85 g (70%), m.p. 121.5–122.0 °C. Found (%): C, 34.68; H, 1.79; N, 11.48; S, 25.91. $C_7H_4N_2O_4S_2$. Calculated (%): C, 34.42; H, 1.65; N, 11.47; S, 26.25. MS (EI, 70 eV), *m/z*: 244 $[M]^+$.

X-ray structural analysis of the crystal solvate 2b · $2C_6H_4Cl_2$. The crystals of $C_{83}H_{21}Cl_4NO_3S$ (M = 1253.87) are monoclinic; at 148 K $a = 17.641(4)$ Å, $b = 14.693(3)$ Å, $c = 19.363(5)$ Å, $\beta = 92.55(2)°$, $V = 5014(2)$ Å^3, $Z = 4$, space group $P2_1/c$, $d_{calc} = 1.661$ g cm^{-3}, $F(000) = 2536$. The unit cell parameters (determined with the use of 24 reflections in the region of $26 \le 2\theta \le 28°$) and intensities of 12,170 independent reflections were measured on an automated four-circle Siemens P3/PC diffractometer (148 K, Mo-Kα radiation, graphite monochromator, θ/2θ-scanning technique, $\theta \le 28°$).

The structure was solved by the direct method. All nonhydrogen atoms were revealed from the difference Fourier maps and refined first isotropically and then anisotropically by the least-squares method. One solvate *o*-dichlorobenzene molecule is disordered between two positions with an occupancy ratio of 4 : 1. All hydrogen atoms (except for those of the *o*-dichlorobenzene molecule with the lower occupancy) were revealed from the difference Fourier synthesis and included in the refinement with isotropic thermal parameters. The final values of the *R* factors were as follows: $R_1 = 0.0560$ (based on F for 7827 observed reflections with $I > 2\sigma(I)$) and $wR_2 = 0.1477$ (based on F^2 for a total of 12,170 independent reflections). All calculations were carried out on an IBM PC computer using the SHELXTL PLUS 5 program package (the Gamma Version). The atomic coordinates are given in Table 4.

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