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Twofold Cycloaddition of 2,4,6-Trimethoxy-benzonitrile Oxide to [60]Fullerene

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Abstract: The 22 conceivable regioisomers of isoxazolo-fullerenes are listed, combined with a proposed nomenclature for their addition patterns. Two of them (I*(mm2), I*(2/m)) are impossible on sterical hindrance. The twofold cycloaddition of 2,4,6-trimethoxy-benzonitrile oxide to [60]fullerene yields in a complex mixture of bisadducts **1**. By combined HPLC separations, we isolated 11 fractions, which are distinguishable in their NMR spectra. From comparison of the possible symmetries for isoxazolo-fullerenes and from the spectra of the isolated reaction products **1** can be concluded that some fractions contain two bisadducts. In the end our analytical data corresponds to 16 bisadducts of 20 possible ones. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The interest in the synthesis of double modified fullerene cages springs from the ambition to generate well-defined, three-dimensional building blocks. An easy way to achieve a twofold modification is the cycloaddition on two different [6,6]-bonds of the fullerene. Although the synthesis of fullerene monoadducts is always accompanied by the formation of such bisadducts, only a few groups are engaged in the isolation and characterization of higher fullerene adducts. The main reason for that is the increased number of reaction products as a result of the different possible addition patterns, which is responsible for difficulties in the isolation of the reaction products. But a fundamental understanding of the maximum number of regioisomer bisadducts and their relative stability is important for all work on higher functionalized fullerenes.

The pioneering work in this field was done by A. Hirsch et al.[1a-1c] and S. R. Wilson et al.[2], which investigated bisadducts of C_{60} with symmetrical addends perpendicular to the annellated bond of the fullerene. In these cases up to eight different regioisomers are conceivable (nine if the two addends are not identical), if only the more reactive [6,6]-bonds are involved in the reaction. The investigations showed, that two up to five main products occur, which belong to varied isomers depending on the reaction type. Only a few examples are known, where the exact structure of the products was determined by

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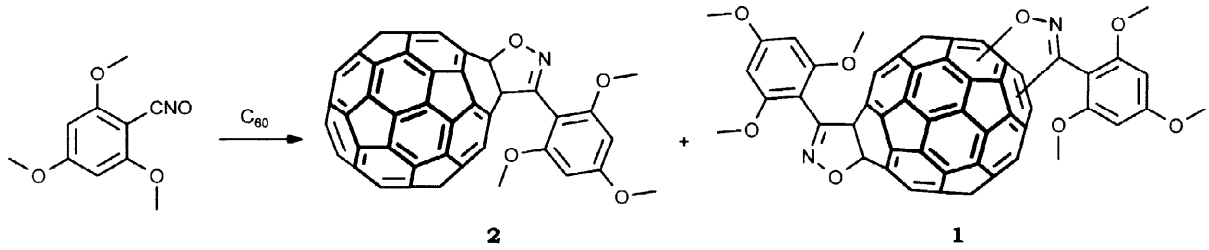
X-ray analysis.[3a-b] In the work of the Hirsch and Wilson groups this assignment is based on NMR and UV experiments and the elution sequence of the reaction products.

In the last years isoxazolo-fullerenes obtained by cycloaddition of nitrile oxides or trimethylsilylnitronates to [60] and [70]fullerene have been studied extensively.[4a-4r] The loss of mirror symmetry perpendicular to the annellated bonds of the fullerene in the RCNO addends leads to additional possibilities for the relative orientation of the substituents R. An attempt to separate a mixture of bisadducts by M. S. Meier and D. J. Rice et al. by means of GPC and buckyclutcher®-HPLC was not very effective.[4e-4f] They investigated the bisadducts of benzonitrile oxide on C_{60} and obtained three partly shouldered fractions. Photodiode array detection indicated impure fractions with at least six up to eight isomers altogether. The isomers were not isolated. No considerations about the theoretical number of possible bisadducts were made and hitherto no other investigations into nitrile oxide bisadducts have been published.

In this work we show the separation of bisadducts **1**, which could be obtained by cycloaddition of 2,4,6-trimethoxy-benzonitrile oxide to [60]fullerene besides the monoadduct **2**. We propose indications for the total number of conceivable addition patterns in isoxazolo-fullerenes and similar unsymmetrical bisadducts in extension of the existing nomenclature for the symmetrical ones.



2 **1**

RESULTS AND DISCUSSION

Nomenclature

In the meantime an efficient nomenclature exists for fullerenes and their compounds.[5] For the practical use however, shorter names for bisadducts based on their addition pattern are desirable. For symmetrical addends A. Hirsch et al. proposed a nomenclature, which was used extensively.[1a] In the end A. Hirsch et al. simplified the descriptors[6], after F. Diederich et al.[7] and the Hirsch group itself[8] had extended the nomenclature to mixed bisadducts. The addition patterns with the two addends on the same hemisphere are named II, III and IV. If they are located on both hemispheres the addition patterns are named I*, II*, III* and IV*. The remaining isomer is named e, where the addends have an equatorial position to each other.

Table 1: Theoretical possible nitrile oxide bisadducts to C_{60} with a II or III addition pattern. The proposed name for each isomer is accompanied by a simplified Schlegel diagram and a 3D model

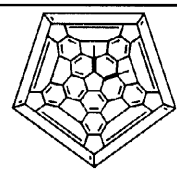
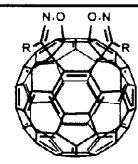
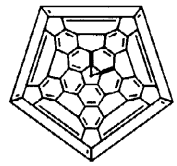
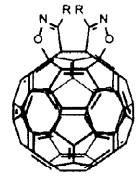
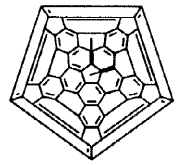
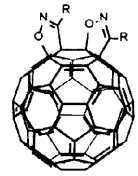
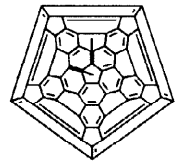
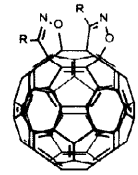
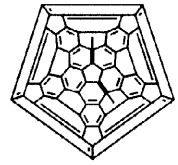
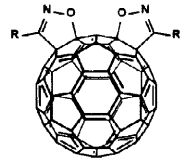
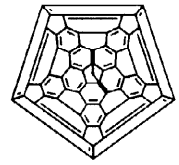
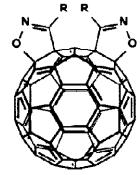
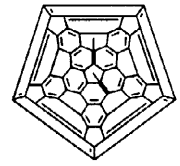
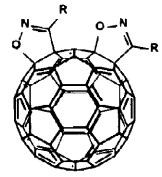
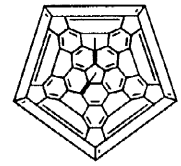
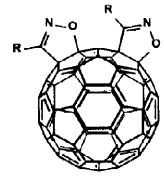
serial number of the diastereomer	addition pattern (A. Hirsch et. al.)	name of the orientation isomer (this work)	Schlegel diagram	3D model
1	II	IIa(m)		
2		IIt(m)		
3		*(R)*-II(1)		
		(S)-II(1)		
4	III	IIIa(m)		
5		IIIt(m)		
6		*(R)*-III(1)		
		(S)-III(1)		

Table 2: Theoretical possible nitrile oxide bisadducts to C_{60} with a IV or e addition pattern. The proposed name for each isomer is accompanied by a simplified Schlegel diagram and a 3D model

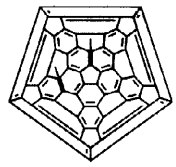
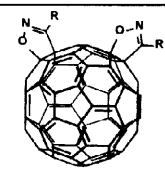
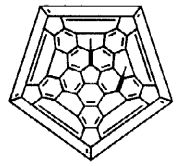
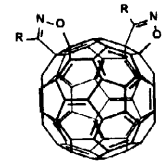
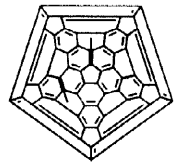
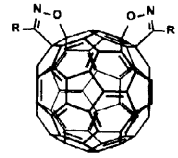
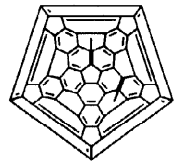
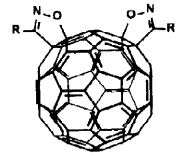
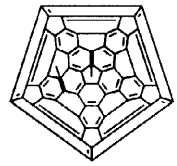
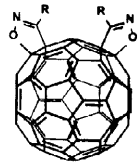
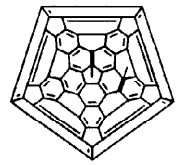
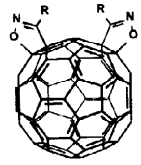
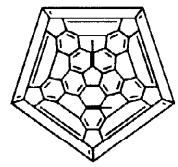
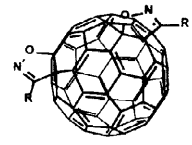
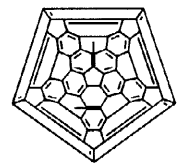
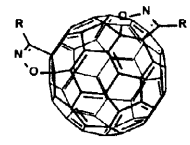
serial number of the dia-stereomer	addition pattern (A. Hirsch et. al.)	name of the orientation isomer (this work)	Schlegel diagram	3D model
7	IV	*(R)*-IV(1)		
		(S)-IV(1)		
8		*(R)*-IVa(2)		
		(S)-IVa(2)		
9		*(R)*-IVt(2)		
		(S)-IVt(2)		
10	e	*(R)*-ea(1)		
		(S)-ea(1)		

Table 3: Theoretical possible nitrile oxide bisadducts to C_{60} with an e, I* or II* addition pattern. The proposed name for each isomer is accompanied by a simplified Schlegel diagram and a 3D model

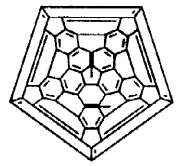
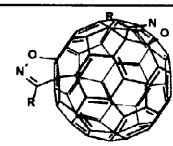
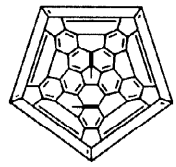
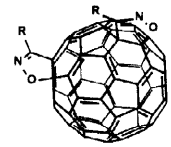
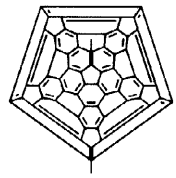
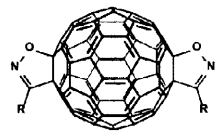
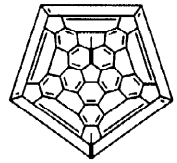
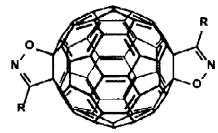
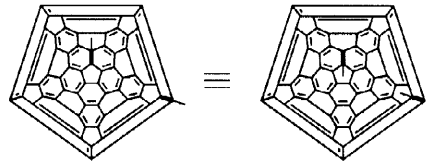
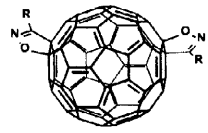
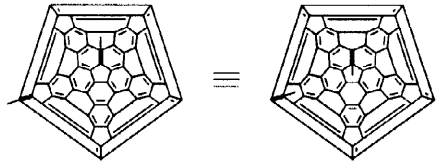
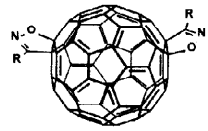
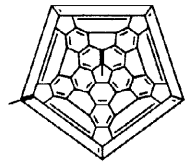
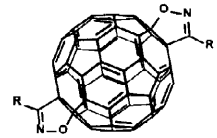
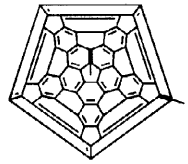
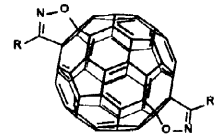
serial number of the diastereomer	addition pattern (A. Hirsch et. al.)	name of the orientation isomer (this work)	Schlegel diagram	3D model
11	e	*(R)*-et(1)		
		(S)-et(1)		
12	I*	I*(mm2)		
13		I*(2/m)		
14	II*	*(R)*-II*(1)		
		(S)-II*(1)		
15		*(R)*-II*av(2)		
		(S)-II*av(2)		

Table 4: Theoretical possible nitrile oxide bisadducts to C_{60} with a II* or III* addition pattern. The proposed name for each isomer is accompanied by a simplified Schlegel diagram and a 3D model

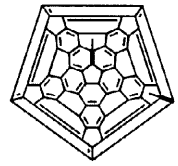
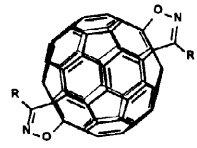
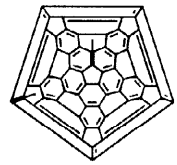
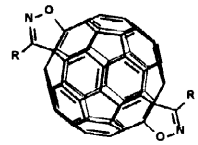
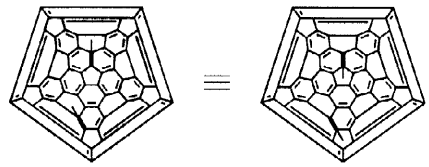
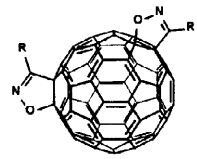
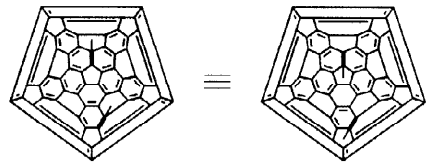
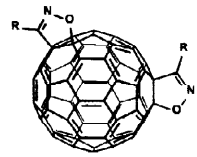
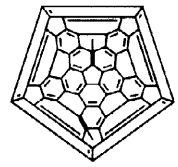
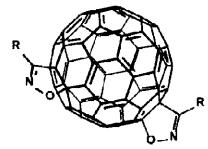
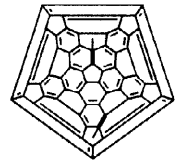
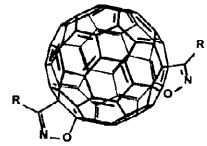
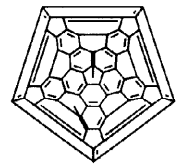
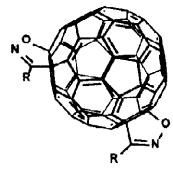
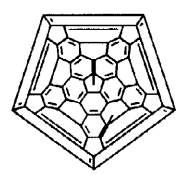
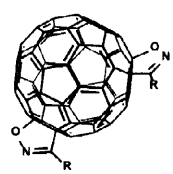
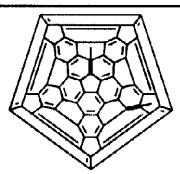
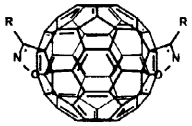
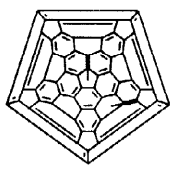
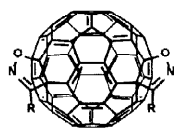
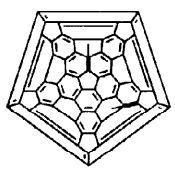
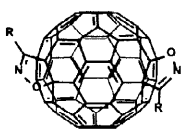
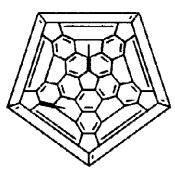
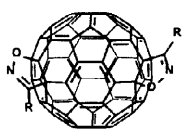
serial number of the diastereomer	addition pattern (A. Hirsch et. al.)	name of the orientation isomer (this work)	Schlegel diagram	3D model
16	II*	*(R)*-II*tv(2)		
		(S)-II*tv(2)		
17	III*	*(R)*-III*(1)		
		(S)-III*(1)		
18		*(R)*-III*av(2)		
		(S)-III*av(2)		
19		*(R)*-III*tv(2)		
		(S)-III*tv(2)		

Table 5: Theoretical possible nitrile oxide bisadducts to C_{60} with a IV* addition pattern. The proposed name for each isomer is accompanied by a simplified Schlegel diagram and a 3D model

serial number of the diastereomer	addition pattern (A. Hirsch et. al.)	name of the orientation isomer (this work)	Schlegel diagram	3D model
20	IV*	IV*a(m)		
21		IV*t(m)		
22		(R)-IV*(1)		
		(S)-IV*(1)		

The isomers IV, II* and III* are inherent chiral. In fullerene monoadducts two sets of e bonds exist. Viewing from an eI bond we can see the face of the annelated ring. Viewing from the eII bond shows us the edge of that ring. For symmetric addends the second addition step yields to the same product for eI and eII, but not in the case if the two addends are unequal.[1c] Also for the unsymmetrical isoxazolo-fullerenes two (chiral) sets of bisadducts with an e addition pattern are possible.

According to this examination in the case of isoxazolo-fullerenes there are 22 constitutional isomers conceivable. 14 of them are chiral and 8 achiral. Tables 1 – 5 describe all of them with both enantiomers if the isomers are chiral. For clarity in the Schlegel diagrams the annellated bonds are drawn thick and the substituent R is symbolized by a short line.

The two dimensional Schlegel diagram is placed aside a three dimensional model for clarification. In the case of the isoxazolo-fullerenes for each addition pattern exists more than one adduct. We propose to use the symmetry of the bisadduct as an additional distinctive feature and add it in brackets in the style of Herrman and Maugin. One isomer each with the addition patterns II, III, IV, II*, III* and IV* is described clearly then. Even both possible isomers with the I* pattern can be told apart.

But in all other cases there are two more regioisomers each, which can not be distinguished. We are therefore compelled to introduce new descriptors and name them a, t, av and tv. Their definition is given in Table 6. If necessary they are inserted between the Hirsch symbol for the pattern and the symmetry.

Table 6: Definition of the four proposed descriptors to name bisadducts of nitrile oxides to C_{60}

de-scriptor	derived from	definition
a	turn *a*way	The two substituents R are turned away from each other.
t	turn *t*o	The two substituents R are turned to each other.
av	turn *a*way from *v*iewer	Viewing along the 2-axis to the hemisphere, where the addends are located, the two vectors of the C→R-bonds are turned away from the viewer.
tv	turn *t*o *v*iewer	Viewing along the 2-axis to the hemisphere, where the addends are located, the two vectors of the C→R-bonds are turned to the viewer.

To distinguish between the enantiomers of the chiral adducts, we propose to place (*R*) and (*S*) in front of the names. Because of the qualitative differences between the enantiomers, we are forced to organize the chiral addition patterns in three groups and give a definition for each group (Table 7). The complete names for the bisadducts are listed in Tables 1 – 5.

It can be easily realized in the structure formulas, that the adducts IIt(m) and IIIt(m) (Table 1) are not possible on steric reasons, because the substituents penetrate each other.

Synthesis and isolation

The synthesis follows our instruction for compound **2**,[4h] in which the amount of nitrile oxide has to be increased to optimize the yield of the bisadducts **1**. To separate these from C_{60} and compound **2**, the latter ones where washed out from the silica gel column with toluene. The exchange of the solvent to toluene/acetonitrile 9 : 1 yields a broad fraction of the bisadducts **1**, which was concentrated and further purified by HPLC on a silica gel column with toluene/acetonitrile 9 : 1. Most fractions of the complex chromatogram were not baseline separated. Therefore another purification step with HPLC on a buckyclutcher I® column (s. phase "X" in lit. [9]) was applied to each fraction. Four of them could be separated in three or four fractions. For the simple reason that the HPLC separation on silica gel was not perfect, some of the fractions in the buckyclutcher® experiment were identical as ^{1}H NMR experiments showed. Altogether 12 not identical fractions could be obtained in this extensive chromatographic procedure.

Table 7: Proposed definition of (*R*) and (*S*) to name enantiomers of chiral bisadducts of nitrile oxides to C_{60}

	range of definition	definition
(*R*)	II(1), III(1), II*av(2), II*tv(2), IV*(1)	Viewing to the hemisphere, where the addends are located, the vectors of the C→R-bonds are orientated clockwise.
	IV(1), IVa(2), IVt(2), II*(1), III*(1), III*av(2), III*tv(2)	Viewing approximately along the vectors of the CR-bonds, where the fullerene core lies below them, the addend on the right is more distant from the viewer than the left one.
	ea(1), et(1)	Viewing from the eII- to the eI-addend, the substituent R of the eII-addend lies on the right.
(*S*)	II(1), III(1), II*av(2), II*tv(2), IV*(1)	Viewing to the hemisphere, where the addends are located, the vectors of the C→R-bonds are orientated anticlockwise.
	IV(1), IVa(2), IVt(2), II*(1), III*(1), III*av(2), III*tv(2)	Viewing approximately along the vectors of the CR-bonds, where the fullerene core lies below them, the addend on the left is more distant from the viewer than the right one.
	ea(1), et(1)	Viewing from the eII- to the eI-addend, the substituent R of the eII-addend lies on the left.

MS and NMR spectra

For all fractions MALDI TOF MS experiments prove the bisadduct mass. For one smaller fraction only a mass spectrum could be obtained, whereas for all others ^{1}H NMR spectra were recorded. Additionally the three main fractions could be characterized by ^{13}C NMR spectroscopy. To make the interpretation of the NMR spectra easier, Tables 8 and 9 show the expected numbers of signals or integrals for ^{1}H and ^{13}C NMR, respectively. These reflections are based on the assumption, that the two 2,4,6-trimethoxyphenyl groups are not rotating. This can be assumed, because there is evidence in a chiral monoadduct of 2,4,6-trimethoxy-benzonitrile oxide on C_{70} for a not rotating substituent. In this example three signals for the methoxy groups can be found in the NMR experiments, instead of two in the relation 1 : 2 for the rotating case.[4h]

In this connection we take into account, that only the symmetries 1, 2, m, 2/m and mm2 can occur for isoxazolo-fullerene bisadducts. As can be seen, the adducts with 2 and m or 2/m and mm2 symmetry are not distinguishable in the NMR experiment. Therefore we combine them in type 2 and type 3 bisadducts, whereas the 1 symmetrical ones form the type 1 (Tables 8 and 9).

Furthermore we take into consideration, that the chromatographic process did not lead us to a perfect separation of the reaction products. Some fractions could consist of two (or more) reaction products. Tables 8 and 9 additionally show the number of signals and integrals for all possible mixtures of two bisadducts (combined types). It's remarkable, that a type 2/2 mixture in equal parts can not be distinguished from the type 1 adduct. Therefore type 2/2 can be regarded as pseudo type 1.

Table 8: Numbers and integrals of the expected signals in the ^{1}H NMR experiment for pure bisadducts **1** and mixtures of two of them in equal amounts. [a] This type can be regarded as pseudo type 1

		symmetry or type combination	number of signals		detailed relation of the integrals (OCH_3/ArH 4.5 : 1)	
			OCH_3	ArH	OCH_3	ArH
monoadduct **2**		m	2	1	3 : 1.5	1
pure bisadducts **1**	type 1	1	6	4	3:3:3:3:3:3	1:1:1:1
	type 2	2	3	2	3:3:3	1:1
		m	3	2	3:3:3	1:1
	type 3	2/m	2	1	3:1.5	1
		mm2	2	1	3:1.5	1
mixtures of two bisadducts **1** (1:1)	combined types	type 1/1	12	8	3:3:3:3:3:3:3:3:3:3:3:3	1:1:1:1:1:1:1:1
		type 1/2	9	6	3:3:3:3:3:3:3:3:3	1:1:1:1:1:1
		type 1/3	8	5	3:3:3:3:3:3:3:1.5	1:1:1:1:1
		type 2/2[a]	6	4	3:3:3:3:3:3	1:1:1:1
		type 2/3	5	3	3:3:3:3:1.5	1:1:1
		type 3/3	4	2	3:3:1.5:1.5	1:1

Table 10 shows the chemical shifts, numbers and integrals for all distinguishable ^{1}H NMR experiments. For the fractions of the three main products Tables 11 and 12 list the chemical shifts and number of signals in the ^{13}C NMR spectra for the 2,4,6-trimethoxy-phenyl substituent and the fullerene core with the annelated heterocycles, respectively.

From the results of the ^{1}H NMR experiments in Table 10 it is obvious, that in nearly all spectra (fractions 4 - 9 and 11) some signals coincide, as can be seen from their integrals. Comparing the spectra with Table 8, most fractions (1, 4 - 6, 8 - 11) seem to contain a chiral bisadduct or two of type 2 in a ratio 1 : 1. A deviation from the equal mixture in type 2/2 fractions should reveal itself in the integrals of the peaks. Actually in fraction 2 this is the case. It is obvious, that this fraction does not contain a chiral bisadduct, but a mixture of two type 2 adducts 1 : 2 (type 2/2).

In fraction 3 the ratio for the OCH_3 and ArH protons is 4 : 2. Only a type 3/3 mixture explains this result. Because only two bisadducts with a type 3 symmetry are conceivable for isoxazolo-fullerenes, this fraction has to contain the adducts I*(mm2) and I*(2/m) (Table 3). The extremely poor solubility of these adducts corresponds to the expected low polarity. In the ^{1}H NMR experiment their ratio is 1 : 2 in solu-

tion, but some substance has already precipitated. Including the threefold intensity, fraction 7 shows a ratio of 9 : 6 for the OCH_3/ArH protons. This can only be explained with a type 1/2 mixture. The ratio 1 : 1.5 for the type 1/type 2 adducts can be deduced from the integrals. It is adequate, that fractions 2 and 7, which could be recognized as mixtures in the NMR experiments already attracted attention as shouldered fractions.

Table 9: Number of the expected signals for the 2,4,6-trimethoxy-phenyl substituent in the ^{13}C NMR experiment for pure bisadducts **1** and mixtures of them. [a] This type can be regarded as pseudo type 1

		symmetry or type combination	number of signals OCH_3	C, arom.
monoadduct **2**		m	2	4
pure bisadducts **1**	type 1	1	6	12
	type 2	2	3	6
		m	3	6
	type 3	2/m	2	4
		mm2	2	4
mixtures of two bisadducts **1**	combined types	type 1/1	12	24
		type 1/2	9	18
		type 1/3	8	16
		type 2/2[a]	6	12
		type 2/3	5	10
		type 3/3	4	8

For the main fractions 2, 4 and 6 the ^{13}C NMR experiments bear out the ^{1}H NMR results (Tables 11 and 12). Taking into account the double intensities, the ratio for the OCH_3/C, arom. carbons is 6 : 12, which restricts the symmetry to type 1 or pseudo type 1 bisadducts. In fraction 2 the 1 : 2 ratio of the intensities proofs a mixture of isomers and because of that the type 2/2 fraction. The pairs of signals in Table 12 for the quaternary carbon atoms in the fullerene cage and the carbons in the heterocycles in combination with the 56 signals in the fullerene region (taking into consideration the multiple intensities) meets exactly the requirements for 1 symmetrical bisadducts or a mixture of two symmetrical ones.

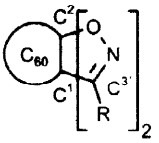
Table 10: Found chemical shifts, numbers and integrals of the signals in the ^{1}H NMR experiment for distinguishable fractions of bisadducts **1** in the HPLC separations

serial number of the fraction	chemical shift (δ) (multiple integrals are indicated)		number of signals (multiple integrals are indicated)		relation of the integrals	
	OCH_3	ArH	OCH_3	ArH	OCH_3	ArH
1	3.56, 3.67, 3.70, 3.76, 3.85, 3.89	6.05, 6.07, 6.17, 6.25	6	4	3:3:3:3:3:3	1:1:1:1
2	3.55, 3.73, 3.78, 3.85, 3.92, 4.00	6.07, 6.11, 6.26, 6.36	6	4	3:6:6:3:6:3	1:2:2:1
3	3.66, 3.73, 3.79, 3.86	6.10, 6.19	4	2	3:6:1.5:3	2:1
4	3.66 (twofold), 3.84, 3.86, 3.91, 4.03	6.16 (twofold), 6.24, 6.32	5 (1 × twofold)	3 (1 × twofold)	3:6:3:3:3	1:2:1
5	3.54, 3.72 (twofold), 3.78, 3.92, 3.99	6.05, 6.10, 6.25, 6.36	5 (1 × twofold)	4	3:6:3:3:3	1:1:1:1:1
6	3.67, 3.72, 3.73 (twofold), 3.79, 3.86	6.09, 6.11, 6.19 (twofold)	5 (1 × twofold)	3 (1 × twofold)	3:3:6:3:3	1:1:2
7	3.45, 3.61, 3.68 (threefold), 3.75, 3.78, 3.88, 4.14	5.98, 6.05, 6.08, 6.09, 6.17, 6.43	7 (1 × threefold)	6	3:4.5:10.5: 4.5:3:3:3	1:1.5:1:1: 1.5:1
8	3.73 (twofold), 3.78, 3.79, 3.86, 3.92	6.09, 6.10, 6.11, 6.19	5 (1 × twofold)	4	6:3:3:3:3	1:1:1:1
9	3.25, 3.71, 3.73, 3.75, 3.80, 4.05	5.98, 6.10 (twofold), 6.25	6	3 (1 × twofold)	3:3:3:3:3:3	1:2:1
10	3.56, 3.67, 3.70, 3.76, 3.85, 3.89	6.05, 6.07, 6.18, 6.25	6	4	3:3:3:3:3:3	1:1:1:1
11	3.33, 3.61, 3.65, 3.70, 3.77, 3.89	6.00, 6.10 (twofold), 6.22	6	3 (1 × twofold)	3:3:3:3:3:3	1:2:1

Table 11: Found chemical shifts and numbers of the signals for the 2,4,6-trimethoxy-phenyl substituent in the ^{13}C NMR experiment for the main fractions of bisadducts **1** in the HPLC separations. The intensities of the signals indicated with [1)] and [2)] have the ratio 1 : 2

serial number of the fraction	chemical shift (δ) (multiple intensities are indicated)		number of signals (multiple intensities are indicated)	
	OCH_3	C, arom.	OCH_3	C, arom.
2	43.76[1)], 54.88[1)], 55.00[1)], 55.07[2)], 55.23[2)], 61.79[2)]	90.77[1)], 90.89[1)], 91.09[2)], 91.11[2)], 97.60[2)], 97.80[1)], 159.56 (twofold), 163.16 (twofold), 163.43 (twofold)	6	9 (3 × twofold)
4	43.60, 54.79, 54.81, 55.06, 55.08, 61.69	91.02 (twofold), 91.04, 91.09, 101.22 (twofold), 159.79, 159.82, 163.48 (twofold), 163.53 (twofold)	6	8 (4 × twofold)
6	54.80, 54.90, 55.17 (twofold), 55.20 (twofold)	90.86, 90.94, 91.01 (twofold), 97.56, 98.02, 159.72 (twofold), 163.16 (twofold), 163.25 (twofold)	4 (2 × twofold)	8 (4 × twofold)

Table 12: Found chemical shifts and numbers of the signals for the fullerene core and the heterocycles in the ^{13}C NMR experiment for the main fractions of bisadducts **1** in the HPLC separations. The intensities of the signals indicated with [1] and [2] have the ratio 1 : 2



serial number of the fraction	C^1	C^2	signals of the fullerene core except C^1 and C^2		$C^{3'}$
			range (see experimental section for details)	number of signals (multiple intensities are indicated)	
2	80.47[2], 80.70[1]	101.13[1], 101.25[2]	134.70 – 149.02	51 (5 × twofold)	149.32[2], 149.62[1]
4	80.22, 80.45	97.77, 97.86	132.88 – 148.98	52 (2 × twofold, 1 × threefold)	149.90, 149.92
6	79.94, 80.34	100.72, 100.85	134.85 – 149.00	51 (3 × twofold, 1 × threefold)	150.97, 151.10

CONCLUSION

Altogether we found eight type 1 fractions and one of type 1/2, type 2/2 and type 3/3 each. Additionally one fraction could only be investigated by mass spectrometry. This corresponds to 14 bisadducts (nine of type 1, three of type 2 and two of type 3) plus a fraction with at least one bisadduct of unknown symmetry. Theoretically 20 bisadducts are conceivable (eight of type 1, ten of type 2 and two of type 3), taking into account that two are sterically impossible. Therefore we have to presume, that at least one of the supposed type 1 fractions is in reality a 1 : 1 mixture of two bisadducts with 2 and/or m symmetry. Finally in the complex reaction mixture eight bisadducts **1** of type 1, five of type 2 and two of type 3 were found. Plus the bisadduct fraction, which was not investigated spectroscopically, this corresponds to 16 bisadducts of 20 conceivable ones. The missing four adducts were not formed or in minor quantities and therefore not collected during the HPLC separations. One or more of the type 1 fractions could be 1 : 1 mixtures of type 2 adducts as well. The reaction yielded in only three main fractions with at least four bisadducts, where fraction 6 with presumable only one adduct makes the main contribution. However the separation from the numerous also formed bisadducts is a costly process. Therefore for future investigations into nitrile oxide bisadducts the limitation of the possible regioisomers by means of e.g. double functional nitrile oxides is advisable.

Without an X-ray analysis, the exact allocation of fraction and bisadduct(s) is not possible. However based on the symmetry information from the ^1H NMR experiments, fraction 3 can be recognized as a

mixture of the two bisadducts with the I* addition pattern (I*(mm2), I*(2/m)). In our opinion an assignment based on the order of elution is too doubtful against the background of the similarity of the isomers and the complexity of the chromatograms. Presumably the clearly improved performance of the HPLC separation in comparison with the work of the Meier/Rice group[4e-4f] is partly based on the gradual chromatography with silica gel and buckyclutcher I® in combination with the introduction of the methoxy substituents. Surely these methoxy groups enhance the interaction of the fullerene adducts with the 2,4-dinitro-phenyloxy groups of the buckyclutcher I® phase.

EXPERIMENTAL

FT-IR: Bruker IFS66; UV-Vis: Hewlett Packard 8452 diode array; ^{1}H and ^{13}C NMR: Bruker AC 300 or DRX 300; FAB-MS: Jeol JMS-700 (positive mode); MALDI TOF MS: Bruker Biflex MALDI-TOF (matrix: 9-nitroanthracene, negative-mode); flash column chromatography: silica gel: Aldrich: 32 – 63 μm, 60 Å; HPLC/UV detection: Abimed Gilson 118, 201, 305, 806; columns: silica gel: Macherey-Nagel: 25 × 250 mm, 7 μm, 50 Å, buckyclutcher I®: Regis Technologies: 21.1 × 250 mm, 10 μm, 100 Å.

1,2:x,y-Bis[3′-(2,4,6-trimethoxy-phenyl)-(epoxynitrilomethino)[60]fullerenes (1)[10]: The synthesis of the bisadducts **1** follows our instruction for compound **2**,[4h]. The ratio of the educts however was adapted to optimize the yield. A typical experiment with 400 mg of C_{60} and 232 mg of the nitrile oxide (1 : 2) yields in 111 mg (28 %) of unused C_{60}, 228 mg (44 %) of the monoadduct **2** and 366 mg of higher adducts. To separate these from C_{60} and compound **2**, the latter ones where washed out from the silica gel column with toluene. The exchange of the solvent to toluene/acetonitrile (9 : 1) yields a broad fraction of the bisadducts **1**, which was concentrated and further purified by HPLC on a silica gel column with toluene/acetonitrile (9 : 1) in portions of 3 ml of a nearly concentrated solution. The separation was optimal with a flow of 6 ml min^{-1}. Some small higher fractions with possibly trisadducts were not collected. Most of the fractions of the complex chromatogram were not baseline separated. Therefore another purification step with HPLC on a buckyclutcher I® column (s. phase "X" in lit. [9]) was applied to each fraction. Four of them could be separated in three or four fractions. To obtain enough material for the spectroscopic analysis, the combined yields of two batches were used. Even then only three fractions supply enough material to record ^{13}C NMR spectra. The combined yields for the single fractions are between 1 and 17 mg.

bisadducts: $C_{80}H_{22}N_2O_8$, mol. mass = 1139.06 g mol^{-1} ;

monoadduct by cycloreversion in the MS experiments: $C_{70}H_{11}NO_4$, mol. mass = 929.86 g mol^{-1}

fraction 0: MS (MALDI TOF): m/z (%): 1140 (6)[M^-], 931 (11)[$C_{70}H_{11}NO_4^-$], 720 (100)[C_{60}^-]

fraction 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56, 3.67, 3.70, 3.76, 3.85, 3.89 (each s, 3 H; OCH_3), 6.05, 6.07, 6.17, 6.25 (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1140 (10)[M^-], 930 (8)[$C_{70}H_{11}NO_4^-$], 721 (100)[C_{60}^-].

fraction 2: IR (KBr): $\tilde{\nu}$ = 480 (m), 524 (m, C_{60}), 560 (m, C_{60}), 637 (m), 814 (m), 1029 (m), 1063 (m), 1129 (s), 1156 (s), 1183 (m, C_{60}), 1205 (m), 1226 (m), 1283 (w), 1342 (w), 1414 (w), 1435 (w, C_{60}), 1460 (m), 1497 (w), 1602 (s, C=N), 1625 (s), 1694 (w), 2851 (w, CH), 2923 (m, CH), 2957 (w, CH) cm^{-1}; UV/Vis ($CHCl_3$): a) d = 1 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 249 (4.92), 297 (4.54), 317 nm (4.48); b) d = 4 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 397 (3.81), 420 (3.65), 491 (3.31), 590 nm (2.73); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (isomer 1), 3.73 (isomer 2), 3.78 (isomer 2), 3.85 (isomer 1), 3.92 (isomer 2), 4.00 (isomer 1) (each s, 3 H; OCH_3), 6.07 (isomer 1), 6.11 (isomer 2), 6.26 (isomer 2), 6.36 (isomer 1) (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.) isomer 1 : isomer 2, 1 : 2; ^{13}C NMR (75 MHz, CS_2/[D_6]acetone 9 : 1, 14 mg, 30842 scans): 43.76, 54.88, 55.00 (each 2 C; OCH_3, isomer 1), 55.07, 55.23, 61.79 (each 2 C; OCH_3, isomer 2), 80.47 (*C*CN, aliphat., isomer 2), 80.70 (*C*CN, aliphat., isomer 1), 90.77, 90.89 (each CH, arom., isomer 1), 91.09, 91.11 (each CH, arom., isomer 2), 97.60 (*C*CN, arom., isomer 2), 97.80 (*C*CN, arom., isomer 1), 101.13 (*C*ON, aliphat., isomer 1), 101.25 (*C*ON, aliphat., isomer 2), 134.70, 135.16, 135.82, 137.12, 139.01, 139.61, 139.65, 140.47, 140.99, 141.20 (2 C), 141.34, 141.35, 141.38, 141.79, 142.32, 143.05, 143.08, 143.19, 143.53, 143.64, 143.76, 143.87, 144.20 (2 C), 144.30, 144.38, 144.49, 144.64, 144.76, 144.79, 144.88, 144.96 (2 C), 145.00, 145.58, 145.60, 146.43, 146.63, 146.78, 146.97, 147.30, 147.33, 147.45, 147.54 (2 C), 147.76, 147.93 (2 C), 147.99, 148.10, 148.40, 148.65, 148.70, 148.83, 149.02 (each C, fullerene), 149.32 (C=N, isomer 2), 149.62 (C=N, isomer 1), 159.56 (2 C, $COCH_3$, arom., 4-position), 163.16, 163.43 (each 2 C, $COCH_3$, arom., 2,6-position), 192.30 (CS_2, solv.) isomer 2 in excess; MS (MALDI TOF): m/z (%): 1140 (20)[M^-], 930 (11)[$C_{70}H_{11}NO_4^-$], 721 (100)[C_{60}^-]; MS (FAB): m/z (%): 1139 (13)[M^+ + H], 1138 (6)[M^+], 930 (9)[$C_{70}II_{11}NO_4^+$], 720 (100)[C_{60}^+]; MS (HR FAB): m/z (± 0.008): 1139.147 [M^+ + H, calcd. 1139.145], 721.010 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,003], 720.008 [C_{60}^+, calcd. 720.000].

fraction 3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 3 H; OCH_3, isomer 1), 3.73 (s, 6 H; OCH_3, isomer 1), 3.79 (s, 3 H; OCH_3, isomer 2), 3.86 (s, 6 H; OCH_3, isomer 2), 6.10 (s, 2 H; CH, arom., isomer 1), 6.19 (s, 2 H; CH, arom., isomer 2), 7.24 (s; $CHCl_3$, solv.), isomer 1 : isomer 2, 2 : 1; MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 930 (38)[$C_{70}H_{11}NO_4^-$], 721 (57)[C_{60}^-].

fraction 4: IR (KBr): $\tilde{\nu}$ = 475 (w), 527 (m, C_{60}), 564 (w, C_{60}), 641 (w), 699 (w), 773 (w), 814 (w), 852 (w), 893 (w), 919 (w), 952 (w), 1029 (w), 1063 (w), 1129 (s), 1156 (s), 1184 (w, C_{60}), 1205 (m), 1226 (m), 1283 (w), 1341 (w), 1414 (w), 1435 (w, C_{60}), 1459 (m), 1498 (w), 1602 (s, C=N), 1625 (s, sh), 2851 (w, CH), 2925 (m, CH), 2957 (w, CH) cm^{-1}; UV/Vis ($CHCl_3$): a) d = 1 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 233 (4.02), 237 (4.02), 249 (3.99), 268 (3.90), 307 (3.66), 362 nm (3.25) ; b) d = 4 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 397 (3.80), 424 (3.54), 469 (3.40), 436 nm (3.32); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6 H; OCH_3), 3.84, 3.86, 3.91, 4.03 (each s, 3 H; OCH_3), 6.16 (s, 2 H; CH, arom.), 6.24, 6.32 (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); ^{13}C NMR (75 MHz, CS_2/[D_6]acetone 9 : 1, 11.7 mg, 19000 scans): 43.60, 54.79, 54.81, 55.06, 55.08, 61.69 (each OCH_3), 80.22, 80.45 (each *C*CN, aliphat.), 91.02 (2 C, CH, arom.), 91.04, 91.09 (each CH, arom.), 97.77, 97.86 (each CON, aliphat.), 101.22 (2 C, *C*CN, arom.), 132.88, 133.73, 134.86,

135.17, 138.05, 139.03, 139.60, 139.63, 140.33, 141.14, 141.45, 141.54, 141.88, 141.99, 142.06 (2 C), 142.49, 142.48, 142.67, 143.12, 143.15, 143.25, 143.36, 143.66 (2 C), 143.67, 143.72, 144.11, 144.34, 144.44, 144.55, 144.73, 144.85, 144.88, 144.97, 145.03, 145.09, 145.45, 145.56, 145.85, 145.90, 145.93, 146.03 (2 C), 146.26, 146.41, 146.70, 146.74, 146.79, 146.97, 147.40, 147.43, 147.62, 148.79, 148.98 (each C, fullerene), 149.90, 149.92 (each C=N), 159.79, 159.82 (each *C*OCH_3, arom., 4-position), 163.48, 163.53 (each 2 C; *C*OCH_3, arom., 2,6-position), 192.30 (CS_2, solv.); MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 930 (28)[$C_{70}H_{11}NO_4^-$], 720 (26)[C_{60}^-]; MS (FAB): m/z (%): 1139 (17)[M^+ + H], 1138 (4)[M^+], 930 (7)[$C_{70}H_{11}NO_4^+$], 720 (100)[C_{60}^+]; MS (HR FAB): m/z (± 0.008): 1140.150 [$^{12}C_{79}{}^{13}CH_{23}N_2O_8^+$, calcd. 1140.148], 1139.143 [M^+ + H, calcd. 1139.145), 1138.136 [M^+, calcd. 1138.138], 931.078 [$^{12}C_{69}{}^{13}CH_{12}NO_4^+$, calcd. 931.080], 930.074 [$C_{70}H_{12}NO_4^+$, calcd. 930,077], 929,042 [$C_{70}H_{11}NO_4^+$, calcd. 929.069], 721.007 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,003], 720.003 [C_{60}^+, calcd. 720.000].

fraction 5: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 3 H; OCH_3), 3.72 (s, 6 H; OCH_3), 3.78, 3.92, 3.99 (each s, 3 H; OCH_3), 6.05, 6.10, 6.25, 6.36 (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1140 (100)[M^-], 930 (68)[$C_{70}H_{11}NO_4^-$], 720 (98)[C_{60}^-].

fraction 6: IR (KBr): $\tilde{\nu}$ = 468 (w), 526 (w, C_{60}), 561 (w, C_{60}), 642 (w), 774 (w), 811 (m), 852 (w), 950 (w), 964 (w), 1030 (m), 1094 (m), 1129 (s), 1156 (s), 1182 (w, C_{60}), 1205 (m), 1226 (m), 1262 (w), 1278 (w), 1341 (w), 1413 (m), 1435 (w, C_{60}), 1457 (m), 1496 (w), 1586 (s, C=N), 1602 (s, C=N), 1625 (m, sh), 2851 (w), 2924 (m), 2957 (w) cm^{-1}; UV/Vis ($CHCl_3$): a) d = 0.1 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 232 (5.02), 250 (4.98), 277 (4.78), 322 nm (4.60); b) d = 4 cm: λ_{max} (lg $\varepsilon/\varepsilon_0$): 393 (3.75), 415 (3.64), 437 (3.56), 484 nm (3.24); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67, 3.72 (each s, 3 H; OCH_3), 3.73 (s, 6 H; OCH_3), 3.79, 3.86 (each s, 3 H; OCH_3), 6.09, 6.11 (each s, 1 H; CH, arom.), 6.19 (s, 2 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); ^{13}C NMR (125 MHz, CS_2/[D_6]acetone 9 : 1, 16.6 mg, 28000 scans): 54.80, 54.90 (each OCH_3), 55.17, 55.20 (each 2 C, OCH_3), 79.94, 80.34 (each *C*CN, aliphat.), 90.86, 90.94 (each CH, arom.), 91.01 (2 C, CH, arom.), 97.56, 98.02 (each *C*CN, arom.), 100.72, 100.85 (each *C*ON, aliphat.), 134.85, 136.36, 136.62, 137.87, 138.78, 138.83, 140.18, 140.76, 141.37, 141.44, 141.59, 141.92, 142.07, 142.28, 142.38, 142.42, 142.57, 142.66, 143.05, 143.45, 143.47, 143.60, 143.78, 144.19, 144.23, 144.30, 144.37, 144.40, 144.48, 144.49, 144.52, 144.70, 145.04, 145.28, 145.58, 145.87, 146.14, 146.18, 146.25, 146.47, 146.63, 146.85, 146.90, 146.91, 147.57, 147.65, 148.09, 148.13, 148.18, 148.36, 149.00 (each C, fullerene), 150.97, 151.10 (each C=N), 159.72 (2 C; *C*OCH_3, arom., 4-position), 163.16 163.25 (each 2 C; *C*OCH_3, arom., 2,6-position), 192.30 (CS_2, solv.); MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 930 (40)[$C_{70}H_{11}NO_4^-$], 720 (50)[C_{60}^-]; MS (FAB): m/z (%): 1139 (9)[M^+ + H], 1138 (2)[M^+], 930 (5)[$C_{70}H_{11}NO_4^+$], 720 (100)[C_{60}^+]; MS (HR FAB): m/z (± 0.008): 1140.146 [$^{12}C_{79}{}^{13}CH_{23}N_2O_8^+$, calcd. 1140.148], 1139.148 [M^+ + H, calcd. 1139.145], 721.007 [$^{12}C_{59}{}^{13}C^+$, calcd. 721,003], 720.001 [C_{60}^+, calcd. 720.000].

fraction 7: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3 H; OCH_3, isomer 1), 3.61 (s, 3 H; OCH_3, isomer 2), 3.68 (s, 6 H; OCH_3, isomer 1 + 3 H; OCH_3, isomer 2), 3.75 (s, 3 H; OCH_3, isomer 2), 3.78 (s, 3 H; OCH_3, isomer 1), 3.88 (s, 3 H; OCH_3, isomer 1), 4.14 (s, 3 H; OCH_3, isomer 1), 5.98 (d, ^4J = 1.9 Hz, 1 H; CH, arom., isomer 1), 6.05 (d, ^4J = 2.2 Hz, 1 H; CH, arom., isomer 2), 6.08 (m, 1 H; CH, arom., isomer 1), 6.09 (m, 1 H; CH, arom., isomer 1), 6.17 (d, ^4J = 2.2 Hz, 1 H; CH, arom., isomer 2), 6.43 (d, ^4J = 1.9 Hz, 1 H; CH, arom., isomer 1), 7.24 (s; $CHCl_3$, solv.), isomer 1/isomer 2 1 : 1.5; MS (MALDI TOF): m/z (%): 1139 (47)[M^-], 929 (34)[$C_{70}H_{11}NO_4^-$], 720 (100)[C_{60}^-].

fraction 8: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 6 H; OCH_3), 3.78, 3.79, 3.86, 3.92 (each s, 3 H; OCH_3), 6.09, 6.10, 6.11, 6.19 (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 930 (52)[$C_{70}H_{11}NO_4^-$], 720 (90)[C_{60}^-].

fraction 9: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25, 3.71, 3.73, 3.75, 3.80, 4.05 (each s, 3 H; OCH_3), 5.98 (m, 1 H; CH, arom.), 6.10 (d, ^4J = 1.8 Hz, 2 H; CH, arom.), 6.25 (d, ^4J = 1.8 Hz, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1140 (100)[M^-], 930 (48)[$C_{70}H_{11}NO_4^-$], 720 (84)[C_{60}^-].

fraction 10: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56, 3.67, 3.70, 3.76, 3.85, 3.89 (each s, 3 H; OCH_3), 6.05, 6.07, 6.18, 6.25 (each s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 929 (50)[$C_{70}H_{11}NO_4^-$], 720 (78)[C_{60}^-].

fraction 11: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.33, 3.61, 3.65, 3.70, 3.77, 3.89 (each s, 3 H; OCH_3), 6.00 (s, 1 H; CH, arom.), 6.10 (s, 2 H; CH, arom.), 6.22 (s, 1 H; CH, arom.), 7.24 (s; $CHCl_3$, solv.); MS (MALDI TOF): m/z (%): 1139 (100)[M^-], 929 (52)[$C_{70}H_{11}NO_4^-$], 720 (69)[C_{60}^-].

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10. The name follows the recommendations for the nomenclature of fullerenes and their compounds.[5] The bridge nomenclature is easier to apply for bisadducts, while we prefer a fusion nomenclature for the monoadducts. Compound **2** should be named 3′-(2,4,6-trimethoxy-phenyl)-isoxazolo[4′,5′:1,2][60]fullerene.