Bis(4-nitrophenyl)tetrafluorosulfuranes: Synthesis, Isomerization and Structural Characterization

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Abstract: Due to their octahedral symmetry, otherwise not available for carbon based chemistry, hypervalent sulfur fluorides are very attractive as structural building blocks for functional organic materials. Direct fluorination offers a convenient access to multigram quantities of highly stable bis(4-nitrophenyl)-tetrafluorosulfurane. Guided by molecular modeling, a novel catalytic process was devised to isomerize the predominantly formed cis isomer to the pure trans isomer.

Starting from the highly stable and kinetically inert sulfur hexafluoride (SF_6),[1] replacement of one fluorine atom by an aromatic ring leads to pentafluorosulfuranyl benzene derivatives, which have been extensively studied by Sheppard at the beginning of the 1960s.[2,3] With few exceptions,[4] further systematic work was impeded by the inconvenient access to this substance class. This changed when recently the pentafluorosulfuranyl *o*- and *m*-nitrobenzenes became available in bulk quantities by a new technology based on the direct fluorination of bis(nitrophenyl)disulfanes.[5] Our interest in hypervalent sulfur fluorides was revived when it was found that the pentafluorosulfuranyl group allows the design of strongly polar liquid crystals[6] which are compatible with active matrix liquid crystal display (AM-LCD) technology.[7] Taking advantage of the octahedral geometry of hypervalent sulfur fluorides, the usefulness of the linear *trans*-tetrafluorosulfuranyl link not only as a potential structural building block for liquid crystals but also for polymers and other functional materials is explored.

The pentafluorosulfuranyl group is the only organo-substituted hypervalent sulfur fluoride that has been studied with a focus on the chemistry of the "organic" part of the molecule.[2]

Nevertheless, there are some examples of simple aliphatic or fluoroaliphatic moieties linked by a tetrafluorosulfuranyl group, which were obtained in small quantities, e.g., by treatment of the corresponding thioethers with ClF[8] or CF_3OF[9] at low temperatures, or by reaction of chlorotetrafluoro(trifluoromethyl)sulfurane with alkenes.[10] Characterization of the possible cis and trans isomers resulting from the octahedral environment of the hypervalent sulfur atom was possible only by spectroscopic methods. For tetrafluorosulfuranyl linked aromatic moieties only circumstantial evidence has been reported, and therefore they were widely considered as an unstable species, especially with regard to hydrolysis.[11]

The approach to larger quantities of tetrafluorosulfuranyl linked aromatic building blocks was based on direct fluorination of the corresponding bis(aryl)sulfide, substituted by *p*-nitro groups to deactivate the aromatic moiety against reaction with fluorine. A suspension of bis(4-nitrophenyl)sulfide **2**[12] in dry acetonitrile was treated with an excess of 10% fluorine in nitrogen at −5 to +2 °C. The reaction is only mildly exothermic, below ca. −7 °C no reaction occurs at all, and above ca. +5 °C increased formation of tarry side products is observed. To trap traces of water and hydrofluoric acid, sodium fluoride, dried in vacuo at 250 °C, was added to the mixture. After workup and recrystallization, as described in the Experimental Section, 80% of a mixture of 15% *trans*-**1** and 85% *cis*-**1** was obtained. Before recrystallization, the major impurity was bis(4-nitrophenyl)sulfone. The supposed intermediate, the difluorosulfane linked compound, or the corresponding sulfoxide was never detected even during the course of the reaction, which was monitored by GC-MS. The product mixture decomposes above 180 °C, and has no pronounced sensitivity against hydrolysis.[13]

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The identity of the two components of the mixture was confirmed by elemental analyses and ^{19}F NMR spectrometry (see also the Experimental Section): *trans*-**1** displays a singlet at 48.1 ppm and *cis*-**1** two triplets at 43.5 and 14.4 ppm.

Mass spectrometry (GC-MS, electron impact (EI), for details see the Experimental Section) displays for both isomers the molecular ion m/z 352 [M$^+$], and its daughter ion m/z 333 [M$^+$ − F] with smaller intensity. This fragment is assumed to correspond structurally to the bis(4-nitrophenyl)trifluorosulfura-nonium cation (**4**$^+$), which seems to be a quite stable species. Most surprisingly, the EI-MS also showed a large difference between *cis*-**1** and *trans*-**1**: For *cis*-**1** an additional peak with m/z 276 [C$_{12}$H$_8$N$_2$O$_4$S$^{\bullet +}$] is observed with varying intensity, which does not occur in the spectrum of *trans*-**1**. Linked scan and MS-MS experiments show that m/z 276 is not a daughter ion of [M$^+$], [M$^+$ − F], or any other ion. Comparison with the mass spectrum of a sample of **2** indicated clearly that this substance and m/z 276 have an identical structure. Since the presence of **2** as contaminant in the MS sample was definitely excluded, we believe that *cis*-**1** is reductively defluorinated in the mass spectrometer, possibly by contact with metal surfaces either at the GC-MS interface or in the ion source. *trans*-**1** seems to be more resistant toward this kind of reductive defluorination. This assumption was also supported by measurement in an ion trap mass spectrometer where *cis*-**1** and *trans*-**1** displayed identical fragmentation patterns.

Slow crystallization from 1,2-dichlorobenzene yielded crystals of pure *trans*-**1**, which were suitable for an X-ray structure analysis.[14] As expected, the two aromatic rings are connected by the *trans*-tetrafluorosulfuranyl link in a perfectly linear way. The distance between C1 of the benzene subunits is 366 pm. This is quite similar to the distance of 401 pm for the acetylene-linked benzenes in tolane (diphenylacetylene), which is a common structure element of liquid crystals and polymers. The *p*-nitrobenzene moieties are aligned in a coplanar manner, resulting in an approximate D_{2h} symmetry of the molecule. The F1−S1−F2 angle is only slightly compressed to 89.44(11)° by the steric pressure from the aromatic subunits.

Crystals of pure *cis*-**1** were obtained by treating the isomer mixture with hot toluene, filtering off undissolved *trans*-**1** and subsequent crystallization at room temperature. The molecular unit in the elementary cell is asymmetric (C_1) and does not have the propeller-like C_2 symmetry as might be expected. Due to mutual repulsion of the aromatic subunits, the C1−S1−C7 angle is broadened to 97.34°. Also, the axial fluorine atoms F1 and F3, as well as the equatorial F2 and F4 atoms, are pushed forward slightly by the bulky benzene moieties (see Scheme 3.) The equatorial S−F$_{eq}$ bond lengths (161.5(2), 162.9(2) pm) are elongated by ca. 2 pm in comparison to the axial ones (159.9(2), 160.7(2) pm.)

(13) Extended storage in acetonitrile solution at room temperature does not result in any significant change in the isomer ratio, which would indicate either a strongly preferred hydrolysis of the sterically more strained *cis*-**1** or a spontaneous isomerization, as one of the referees suggested.

(14) (a) Crystal structure data for *trans*-**1** (C$_{12}$H$_8$F$_4$O$_4$S): monoclinic, $P2_1$/c, a = 6.410(4) Å, b = 11.370(4) Å, c = 9.627(5) Å, β = 108.00(4)°, V = 667.3(6) Å^3, Z = 2, ρ_{calcd} = 1.753 g·cm^{-1}, $R(F)$ = 4.31% for 1066 observed independent reflections (6.68° ≤ 2θ ≤ 50.00°). (b) *cis*-**1** (C$_{12}$H$_8$F$_4$O$_4$S): monoclinic, $P2_1$/c, a = 8.105(5) Å, b = 13.526(4) Å, c = 12.166(5) Å, β = 92.57(4)°, V = 1332(1) Å^3, Z = 4, ρ_{calcd} = 1.756 g·cm^{-1}, $R(F)$ = 4.60% for 2604 observed independent reflections (4.50° ≤ 2θ ≤ 51.96°). (c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-116710 (*trans*-**1**) and No. CCDC-116711 (*cis*-**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

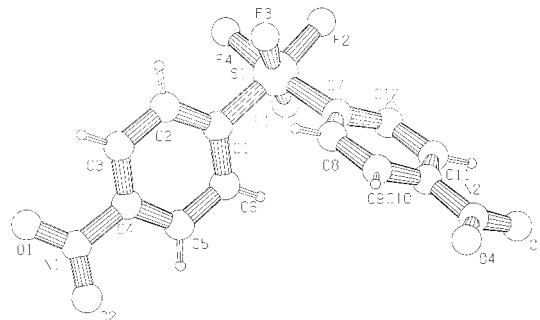**Scheme 1.** Synthesis of the Building Block **1**^{a}
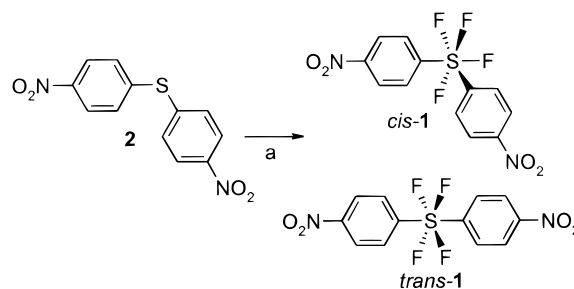
^{a} 10% F$_2$/N$_2$, CH$_3$CN; −5 → 2 °C (80%; mixture of *trans*-**1** and *cis*-**1**, 15:85).

Scheme 2. X-ray Structure of *trans*-**1**^{a}
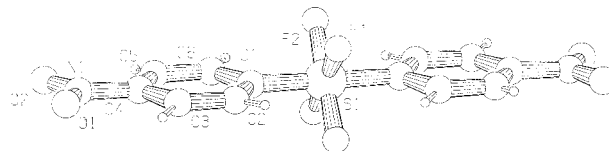
^{a} Approximate D_{2h} symmetry of the molecular unit, S1−F1 161.90(18) pm, S1−F2 162.7(2) pm, C1−S1 183.3(4) pm, F1−S1-F2 89.44(11)°.

Scheme 3. X-ray Structure of *cis*-**1**^{a}

^{a} C_1 Symmetry of the molecular unit, C1−S1 182.4(3) pm, S1−C7 182.2(3) pm, S1−F1 160.7(2) pm, S1−F3 159.9(2) pm, S1−F2 161.5(2) pm, S1−F4 162.5(2) pm, C1−S1−C7 97.34°, F1−S1−F3 173.91°, F2−S1−F4 84.72°, C2−C1−S1−F3 38.25°, F3−S1−C7−C8 43.9°.

Scheme 4. Calculated Heats of Formation for Different Conformers (D_{2h} and D_{2d}) and Isomers (C_1) of Diphenyltetrafluorosulfurane (**3**), Relative to the D_{2d} Conformer Which Is Thermodynamically the Most Stable^a
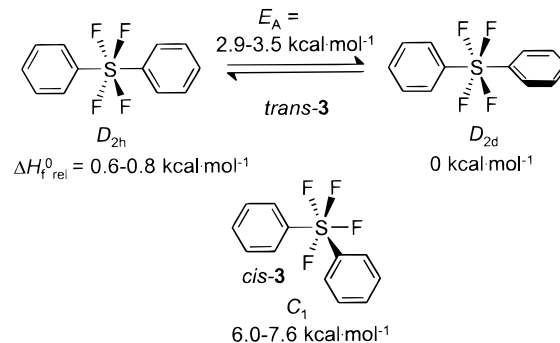
^{a} The exact energies depend on the level of theory applied for the calculation.

Unfortunately, the major part (85%) of the product mixture consisted of the cis isomer which was only of limited interest with regard to liquid crystal synthesis. Variation of the reaction temperature within the narrow possible limits (between ca. −5 and +5 °C) did not influence the isomer ratio. Performing the reaction without the dry sodium fluoride resulted only in

Scheme 5. Calculated Activation Enthalpies E_A for the Uncatalyzed (above) and "fluorophilically" Catalyzed (below) Isomerization of SF_6 and SF_5^+, Respectively[a]
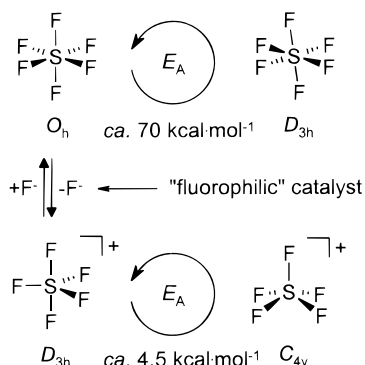
[a] The exact energies depend on the level of theory applied for the calculation.

Scheme 6. Isomerization of the Mixture of *cis/trans*-**1**[a]
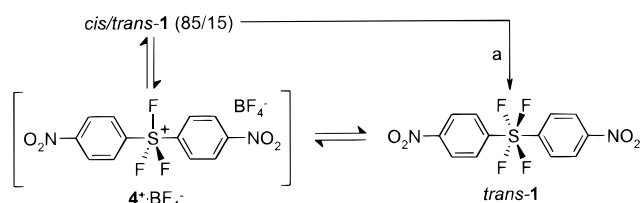
[a] (1) Catalyst $BF_3 \cdot OEt_2$, CH_2Cl_2; room temperature, 1 h; (2) Me_3SiOMe; room temperature, 10 min (87% pure *trans*-**1**).

increased sulfone formation. Preferred formation of the sterically more crowded *cis*-tetrafluorosulfuranyl link has also been observed after treatment of (fluoro)aliphatic thioethers with ClF,[8] and there is up to now no completely satisfactory explanation for the mechanism. Since chromatographic separation on a larger scale was severely impeded by the low solubility of the mixture in the eluent (e.g. trichloroethylene), it was decided to look for a way to convert *cis*-**1** into *trans*-**1**.

Ab initio and density functional calculations[15] on diphenyltetrafluorosulfurane (**3**) as a model compound showed that the trans isomer should be preferred by 6.0 kcal·mol^{-1} (HF/6-31G*//HF/6-31G* + ZPE) and 7.6 kcal·mol^{-1} (B3LYP/6-31G*//B3LYP/6-31G* + ZPE) over the cis form, respectively. The trans isomer can exist in two different conformations: the D_{2h} conformer with coplanar benzene rings, and the D_{2d} conformer where the aromatic rings are oriented perpendicular to each other. As the calculation indicates, the D_{2d} conformer of *trans*-**3** is preferred by 0.6 kcal·mol^{-1} at the HF and 0.8 kcal·mol^{-1} at the DFT level of theory, and the rotational barrier is 3.5 (HF) and 2.9 kcal·mol^{-1} (DFT), respectively. In the transition structure (C_1), one benzene unit is staggered with respect to the equatorial

(15) (a) SPARTAN Version 5.1, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612. (b) Gaussian 98, Revision A.6, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1998. All stationary points were characterized as minima (zero imaginary frequencies) or transition structures (one imaginary frequency) by calculation of vibrational frequencies. All energies were corrected for the (unscaled) zero-point vibrational energy (ZPE).

fluorine atoms and the other is eclipsed. Thus, in crystalline *trans*-**1** the energetically slightly disfavored D_{2h} conformer seems to be preferred because of crystal packing effects.

The first possibility investigated was thermal isomerization: To obtain some estimate on the principal feasibility of this concept, sulfur hexafluoride was chosen as a model compound to perform some calculations on the configurational stability of hypervalent sulfur fluorides. For octahedral coordination (O_h symmetry) the changing of ligand positions by a "turnstile" mechanism has to proceed via a trigonal prismatic (D_{3h}) transition state. Ab initio calculations[15] indicated an activation barrier of 68.7 (B3LYP/6-31G*//B3LYP/6-31G* +ZPE) and 74.1 kcal·mol^{-1} (MP2/6-31G*//MP2/6-31G* + ZPE) for the (degenerated) thermal isomerization of SF_6 via a trigonal prismatic transition state. Therefore, it was concluded that thermal decomposition would be a more probable reaction path than a clean isomerization at elevated temperatures.[16]

While sulfur hexafluoride displays an extreme configurational stability, the inversion barrier for pentavalent phosphorus (PF_5) is known to be far lower. Even at room temperature fast scrambling of the fluorine positions by Berry pseudorotation takes place.[17] A reasonable approach to take advantage of this fact for the isomerization problem would be the temporary removal of a fluoride ion from the coordination sphere of the hypervalent sulfur to obtain the isoelectronic SF_5^+ cation, or the respective organo derivative. For the model system the isomerization barrier of ca. 70 kcal·mol^{-1} for SF_6 would be reduced to only 4.2 (DFT) and 4.9 kcal·mol^{-1} (MP2) for the isomerization of SF_5^+ (D_{3h}) via a tetragonal pyramidal (C_{4v}) transition state. An isomerization with such a low activation energy would be expected to proceed fast enough for preparative purposes even at room temperature.

How is fluoride abstracted from **1** in a reversible manner? Seppelt and co-workers[11] decribed the preparation and NMR spectroscopic study of $R-SF_4^+$ cations in solution by reaction of a variety of organic pentafluorosulfuranyl derivatives with the strong Lewis acid SbF_5. The tendency of arylpentafluorosulfuranyl[6] and bis(aryl)tetrafluorosulfuranyl derivatives to form the corresponding sulfuranonium cations is also indicated by the prominent $[M^+ - F]$ peak obtained by EI mass spectrometry. Due to possible resonance stabilization, bis(aryl)trifluorosulfuranonium cations are expected to be even more stable and easier to create than aryltetrafluorosulfuranonium ions.

The assumption proved to be correct, and treatment of a solution of *cis/trans*-**1** in dichloromethane with 0.1 equiv of boron trifluoride etherate at room temperature resulted in complete conversion to the thermodynamically more stable *trans*-**1** within a few minutes (see the Experimental Section). The key process of this "fluorophilic" catalysis is presumably the reversible formation of bis(4-nitrophenyl)trifluorosulfuranonium tetrafluoroborate ($4^+ \cdot BF_4^-$) which rapidly equilibrates to the trans form.[17] The only side reaction is the formation of small amounts of the corresponding sulfone, probably by hydrolysis of the sulfuranonium cation. In contrast to the complete kinetic deactivation of hypervalent sulfur fluorides against hydrolysis, the sulfuranonium cation has lost its protecting fluorine shield. Pure *trans*-**1** is an even more stable substance than the isomer mixture: it melts under decomposition at 249 °C, and its sensitivity toward hydrolysis is comparable to that of 4-nitropentafluorosulfuranyl benzene.

(16) A similar conclusion was reached by: Boldyrev, A. I.; Zakzhevskii, V. G.; Charkin, O. P. *J. Structural Chem. (Engl. Transl.)* **1982**, *23*, 844–847. Boldyrev, A. I.; Zakzhevskii, V. G.; Charkin, O. P. *Zh. Strukt. Khim.* **1982**, *23*, 30–34.

(17) Holleman, A. F.; Wiberg, E. *Lehrbuch der Anorganischen Chemie*, 91-100 ed.; Walter de Gruyter: Berlin and New York, 1985; pp 640–642.

By direct fluorination of the corresponding diarylsulfide multigram quantities of a mixture of the cis and trans isomers of bis(4-nitrophenyl)tetrafluorosulfurane **1** can be prepared. Supported by ab initio and DFT calculations on simple model compounds a catalytic process for the isomerization of *cis*-**1** to *trans*-**1** was devised. This "fluorophilic" catalysis gives access to bulk quantities of *trans*-**1** which could serve as an interesting building block for liquid crystals, polymers, or pharmaceuticals.

Experimental Section

1 (isomer mixture: 15% trans/85% cis). A suspension of 20 g (72 mmol) of bis(4-nitrophenyl)sulfide (**2**)[12] and 60 g of NaF (dried in vacuo at 250 °C for 18 h) in dry acetonitrile is cooled to −5 °C. Under vigorous stirring a stream of 10% fluorine in nitrogen is bubbled through the mixture keeping the temperature between −5 and −3 °C until completion of the reaction, as indicated by GC-MS. After the suspension is purged with nitrogen, the solvent is removed under reduced pressure. The solid residue, consisting mainly of NaF, product, and bis(4-nitrophenyl)sulfone, is extracted 5 times with 200 mL portions of hot CHCl₃. The combined extracts are filtered and evaporated down to a volume of 250 mL. After crystallization for 18 h at −20 °C the crude product is isolated by filtration. A second recrystallization from acetonitrile yields 20 g (80%) of yellow crystals, consisting of a mixture of 15% *trans*-**1** and 85% *cis*-**1**: mp >180 °C, dec; correct elemental analysis.

Crystals of the Pure Isomers of 1 for X-ray Structure Analysis. The isomer mixture is dissolved in hot 1,2-dichlorobenzene, and after cooling to room temperature, filtered. After the mixture stands at room temperature for two weeks suitable crystals of pure *trans*-**1** are obtained.

Extraction of the crude isomer mixture with boiling toluene, filtration of the hot solution, and subsequent crystallization at room temperature yields crystals of pure *cis*-**1**: ¹H NMR (300 MHz, CDCl₃, 303 K) δ 7.74 (d, 4H, *J* = 10 Hz), 8.22 (d, 4H, *J* = 10 Hz); ¹⁹F NMR (280 MHz, CDCl₃, 303 K) δ 43.5 (t, 2F, *J* = 99 Hz), 14.4 (t, 2F, *J* = 99 Hz); MS (EI)[18] *m/z* 352.0143 (calcd 352.0141) [M⁺], 333 [M⁺ − F], 192 [O₂NPhSF₂⁺], 146 [PhSF₂⁺], 141 [O₂NPhF⁺], 111 [OPhF⁺], 95 (100%) [PhF⁺]; additional signals with varying intensity: *m/z* 276.0203 (calcd 276.0205) [C₁₂H₈N₂O₄S•⁺], 246 [C₁₂H₈NO₃S⁺], 184 [C₁₂H₈S⁺].

Isomerization to the Trans Isomer 1: A 60 g (0.17 mol) sample of the isomer mixture (*trans*-/*cis*-**1** 15:85) is suspended in 1.8 L of dry CH₂Cl₂ and treated at room temperature with 2.61 mL (17 mmol) of BF₃·Et₂O for 60 min. After addition of 6 mL (44 mmol) of MeOSiMe₃, the suspension is stirred for an additional 30 min and then evaporated to dryness. The crude product is recrystallized twice from acetonitrile. Yield: 52 g (87%) of pale yellow needles: mp 249 °C, dec; ¹H NMR (300 MHz, *d₆*-DMSO, 303 K) δ 8.31 (d, 4H, *J* = 12 Hz), 8.42 (d, 4H, *J* = 12 Hz); ¹⁹F NMR (280 MHz, CDCl₃, 303 K) δ 48.1 (s); MS (EI): [18] *m/z* 352 [M⁺], 333 [M⁺ − F], 192 [O₂NPhSF₂⁺], 146 [PhSF₂⁺], 141 [O₂NPhF⁺], 111 [OPhF⁺], 95 (100%) [PhF⁺].

Supporting Information Available: Detailed results of the calculations on **3**, SF₆, and the SF₅⁺ cation on various levels of theory, and detailed data on the X-ray structure analyses of *trans*-**1** and *trans*-**2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(18) Electron impact (EI) spectra were obtained using a VG AutoSpec mass spectrometer (source temperature 160 °C, electron energy 70 eV, source pressure 10⁻⁹ bar) coupled with a Fisons GC 8000 (column: HP-5 MS 30 m; column temperature: 70−320 °C, 15 °C·min⁻¹; pressure: 1 bar; injector temperature: 260 °C). Elemental compositions of the ions were determined within an average accuracy of ca. 10⁻² Da based on accurate mass measurements of at a resolution of 10000 (10% valley def.) using perfluorokerosene as the reference compound. Metastable ion spectra (*B²/E* linked scan, *B/E* linked scan) were recorded on the same machine. MS-MS spectra were obtained using a Varian Saturn 2000 mass spectrometer (source temperature 220 °C, emission current 15) coupled with a Varian 3400 GC (column: DB-5 30 m; column temperature: 70−320 °C, 15 °C·min⁻¹; pressure: 0.6 bar; injector temperature: 260 °C.)