"parking" population of state Φ_{2+} unaffected. This is achieved by first transferring half of the initial population of Φ_{0+} into the excited state Φ_{2-} and subsequently to Φ_{0-}, which then interferes coherently with the remaining fraction of Φ_{0+} leading to the formation of the target state of the left enatiomer Ψ_{0L}. Finally, the "parking" population of Φ_{2+} is dumped into the excited ($v = 1$) state of the left enantiomer Ψ_{1L}, by means of the fourth and fifth subpulses which create the corresponding coherent superposition of states Φ_{1+} and Φ_{1-}, respectively, without influencing the population of Ψ_{0L}.

The net effect is conversion of the undesirable right portion of the racemate from its torsional ground state to the left enantiomer in its first torsional excited state, while keeping the initial fraction of the desired enantiomer in its torsional ground state. This is accomplished by transferring the incoherent population of two initial states (the racemate) into an incoherent superposition of two coherent states (the left enantiomer), where the coherences in each of the doublet states are introduced by the second to fifth subpulses. After the end of the laser pulses, the pure enantiomer tunnels back and forth towards the opposite enantiomer. Therefore, the resulting enantiomer selectivity remains, however, only for half of the tunneling time ($\tau_1/2$). This time is long enough, however, for subsequent laser control or reactions which may stabilize the target pure enantiomer.[16, 17]

Tunneling is also present during the laser pulse, but it does not impair the final localization, because it is exceedingly slow (630 ps) for Ψ_{0L} and, moreover, the more rapid tunneling of the intermediate excited states Ψ_{1L} and Ψ_{1R} or Ψ_{2L} and Ψ_{2R} compensate each other since their populations are designed to be nearly equal.

In conclusion, a preoriented racemate can be converted into a pure enantiomer by means of linearly polarized laser pulses. In our simulation the temperature is so low that only the lowest doublet of torsional states is populated. Extensions to higher temperatures are however straightforward, and involve transitions to other "parking" states followed by sequential transfers into appropriate excited states of the target enantiomer. Our approach can also be extended to rotating molecules, for example by means of alignment along the P–S axis but allowing free rotation around it.[21] The linear polarized laser pulses which define a left- or right-handed coordinate system in our model case, are then replaced by circular polarized laser pulses. Additional details of this extended general model will be published elsewhere. The present results should also serve as a reference for more complex situations such as the inclusion of the effects of intramolecular vibrational redistribution.

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Bis(pentafluorophenyl)xenon, $Xe(C_6F_5)_2$: A Homoleptic Diorganoxenon Derivative[**]

Nicola Maggiarosa, Dieter Naumann,[*] and Wieland Tyrra

Dedicated to Prof. Dr. Herbert Jacobs
on the occasion of his 65th birthday

In 1989, pentafluorophenylxenon borates were synthesized as first examples of organoxenon derivatives.[1, 2] In the following years, numerous new Xe–C compounds with the structural element $[Xe{-}C]^+$ were synthesized and characterized.[3–8] The only $C_6F_5Xe^{II}$ compounds with two covalent bonds are C_6F_5XeCl, $[(C_6F_5Xe)_2Cl]^+[AsF_6]^-$,[9] and $C_6F_5XeOCOC_6F_5$.[10] The existence of a xenon derivative with two xenon–carbon bonds has not yet been confirmed. Already in 1979, $Xe(CF_3)_2$ was described;[11] however, these results could not be reproduced and are therefore the subject of controversy.

Investigations of the substitution reactions of XeF_2 suggested that the synthesis of a compound containing the fragment C-Xe-C and stable enough for spectroscopic detection should be possible by the reactions of XeF_2 and

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[*] Prof. Dr. D. Naumann, Dr. N. Maggiarosa, Dr. W. Tyrra
Institut für Anorganische Chemie
Universität Köln
Greinstrasse 6, 50939 Cologne (Germany)
Fax: (+49) 221-470-5196
E-mail: d.naumann@uni-koeln.de

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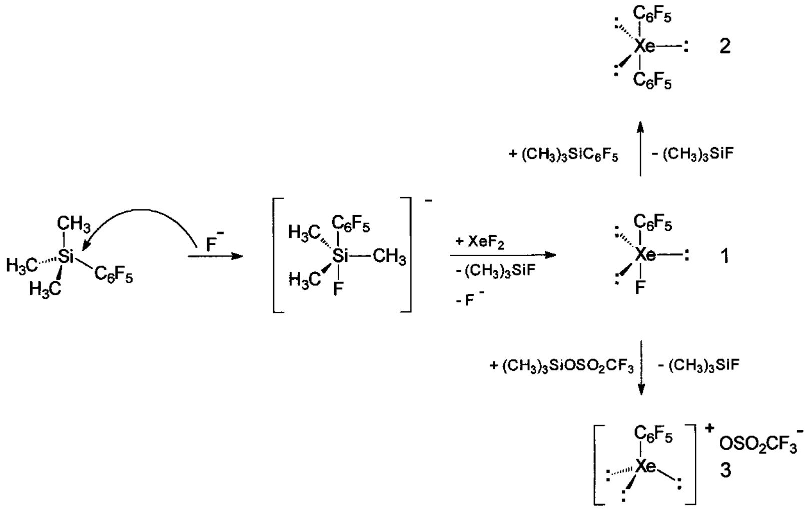
arylsilanes, although in previous reports on similar reactions no concrete spectroscopic evidence for xenon–carbon compounds was mentioned.[5, 12] The reaction of XeF_2 and Me_3SiCF_3 yielded C_2F_6 as the major product, this result can be interpreted in terms of the formation of the intermediate $Xe(CF_3)_2$.[13] Pentafluorophenyl derivatives should exhibit an increased thermal stability compared with non-aromatic perfluoroorganoxenon compounds. For this reason, we investigated the reaction of XeF_2 and $Me_3SiC_6F_5$.



Scheme 1. Synthesis and reactions of **1**.

From the reactions of $Me_3SiC_6F_5/[Me_4N]F$ and XeF_2 in propionitrile, propionitrile/acetonitrile, acetonitrile, or CH_2Cl_2, $Xe(C_6F_5)_2$ (**2**), the first [10-Xe-2] species with two xenon–carbon bonds is formed (Scheme 1) as a colorless solid that decomposes spontaneously at 20 °C. The reactions proceed analogously to the fluoride-initiated trifluoromethylations[14] via the reactive intermediates $[Me_3Si(C_6F_5)F]^-$ and $[Me_3Si(C_6F_5)_2]^-$, respectively. In the course of the reactions, C_6F_5XeF (**1**) is formed as an intermediate which has been characterized by NMR spectroscopy. The by-products formed are $(C_6F_5)_2$ and C_6F_5H, the latter is formed by reactions of **2** and the solvent.

Solutions of **2** in the basic solvent MeCN are rather unstable at −40 °C and decompose quantitatively within 24 h to give $(C_6F_5)_2$ and small amounts of C_6F_5H. Above −20 °C an uncontrolable, spontaneous reaction occurs. In contrast, solutions of **2** either in a mixture of propionitrile/MeCN or in propionitrile, dichloromethane, or [D$_6$]acetone are stable at −65 °C for several days. Above −45 °C a continuous increase in the formation of $(C_6F_5)_2$, C_6F_5H, and C_6F_5D, respectively, was observed. The solubility of **2** is significantly better in MeCN and CD_3CN than in EtCN, CH_2Cl_2, or acetone.

Attempts to prepare **1** as a pure substance have so far been unsuccessful. Compound **1** always contained small quantities of **2** (<5%). The reaction of **1** and $Me_3SiOSO_2CF_3$ yields **3**. This reaction suggests that **3** is an excellent tool for the synthesis of further covalent C_6F_5Xe-R compounds.

Compound **2** reacts with elemental mercury in MeCN between −40 °C and room temperature to give $Hg(C_6F_5)_2$ as well as $(C_6F_5)_2$ and traces of C_6F_5H. All the products are unambiguously identified by their NMR spectra.

The NMR spectra of **2** shows an $[[AC]_2B]_2X$ spin system. The splitting of the $[[AC]_2B]_2$ part is comparable to that of an $[[AZ]_2M]_2$ system. To aid analysis of the ^{129}Xe NMR spectrum, the $[[AZ]_2M]_2$ part of the model substance, $(C_6F_5)_2SiBr_2$,[15] is used, the effects of higher order on the resonance signals of the ^{129}Xe spectrum are small and can be neglected. The absolute values determined from the analysis of the ^{129}Xe NMR spectrum of **2** ([D$_6$]acetone, −58 °C; Figure 1 A) are $^3J(Xe,F) = 45.1$ Hz, $^4J(Xe,F) = 34.7$ Hz, and $^5J(Xe,F) = 9.5$ Hz. The calculated ^{129}Xe NMR spectrum (C) matches well with the measured ones (A and B).

In the ^{19}F NMR spectrum of **1**, the resonance signal of the fluorine atom directly bound to xenon is detected in propionitrile/ MeCN at −58 °C at $\delta = 2.3$ (Figure 2) and in CH_2Cl_2 at $\delta = -1.6$ as a ψ-septet with splittings of 9.8 Hz. In MeCN solution, this signal is detected as a broad resonance at

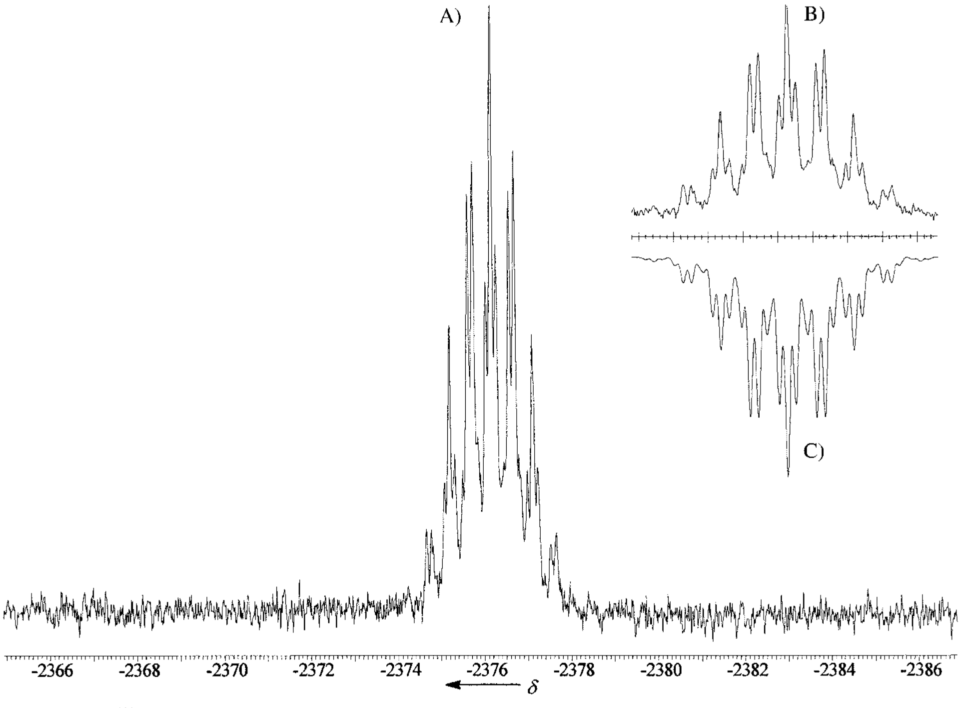


Figure 1. A) ^{129}Xe NMR spectrum of **2** measured in [D$_6$]acetone at −58 °C; B) section of the spectrum determined by experiment; C) corresponding section of the simulated experiment.

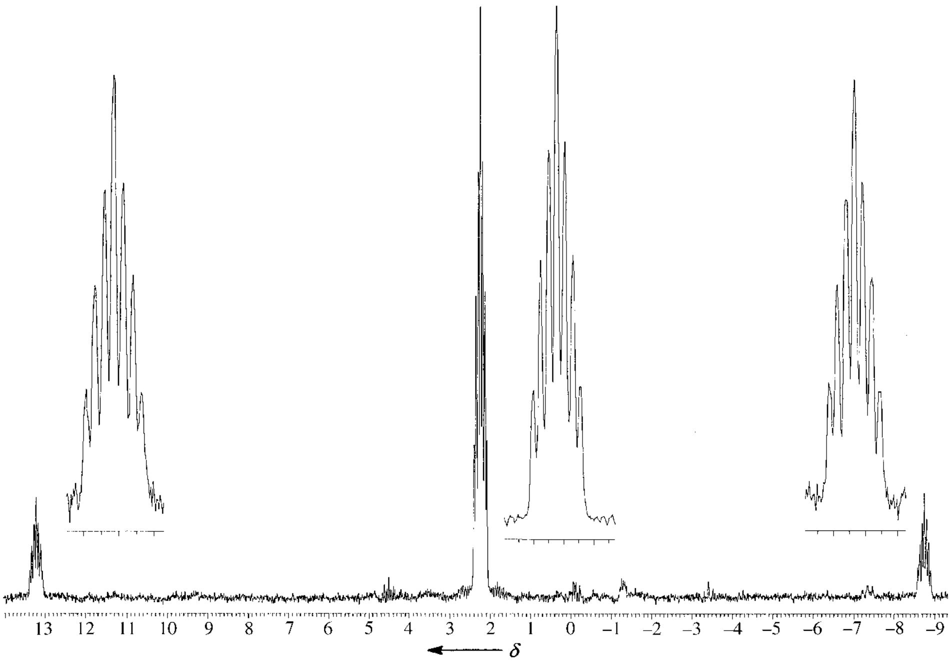


Figure 2. ^{19}F NMR spectrum of **1** (FXe part) in EtCN/MeCN at −58°C.

$\delta = 4.5$ which is converted, after addition of $[Me_4N]F$, into a poorly resolved multiplet with a line width of $\tau_{1/2} = 10$ Hz. This suggests by analogy to the pentafluoroxenate(IV) anion[16] a rapid exchange of the terminal fluorine atom in the basic good-coordinating solvent MeCN. The ^{129}Xe NMR signal of **1** in acetonitrile is detected at $\delta = -2004.3$ and as expected is split into a doublet $^1J(Xe,F) = 4099.6$ Hz of triplets $^3J(Xe,F) = 82$ Hz of multiplets.

The comparison of the ^{19}F and ^{129}Xe NMR spectroscopic data of the ion $[C_6F_5Xe]^+$ (**3**)[1, 2] with that of $C_6F_5XeOCOC_6F_5$,[10] C_6F_5XeCl, $[(C_6F_5Xe)_2Cl][AsF_6]$,[9] **1**, and **2** (Table 1) is noteworthy. With increasing covalency, the resonance signals of the *p*-fluorine are significantly shifted to higher field. This effect is strongly marked by $\Delta\delta \approx 11$ of **2** compared with the cation and $\Delta\delta \approx 5$ and 6, respectively, compared with the unsymmetrically substituted derivatives.

This high-field shift implies a decrease of mesomeric interactions between the C_6F_5 group and the Xe^{II} center.[10] The high-field shift of the ^{129}Xe resonance signal of **2** and the simultaneous low-field shift of the C-1 resonance compared with data of other pentafluorophenylxenon derivatives (Table 1) verify that the effective charge at the xenon atom is significantly lower and at the C-1 atoms is significantly higher than in all the compounds known so far.

Experimental Section

2: XeF_2 (1.10 g, 6.50 mmol) was suspended in a Schlenk tube at −78°C in the appropriate solvent (40 mL, EtCN; EtCN/MeCN (2:1); MeCN (−40°C); CH_2Cl_2). $Me_3SiC_6F_5$ (3.43 g, 2.72 mL, 14.29 mmol) was added. The stirred mixture was warmed to −60°C; with MeCN all manipulations were made at −40°C. To this suspension precooled $[Me_4N]F$ (0.01 g, 0.11 mmol) was added.[14] The mixture was warmed to −40°C for a short period and then cooled to −60°C. A transparent, colorless solution was formed. Additional stirring for 4 h at −60°C led to the formation of **2** as a white precipitate, whereas the educts XeF_2 and $Me_3SiC_6F_5$ vanished completely (^{19}F NMR). To this suspension, with the exception of the solvent MeCN, pentane precooled to −78°C was added to complete the precipitation of **2**. The solution was decanted and the remaining solid was washed several times with pentane. In contrast to **2**, the by-products $(C_6F_5)_2$, Me_3SiF, and C_6F_5H are readily soluble in pentane and are therefore easily removed. The product **2** was dried at 10^{-3} mbar and −50 to −35°C and obtained as a colorless solid. Compound **2** was dissolved in [D$_6$]acetone and investigated by NMR spectroscopy (^{129}Xe, ^{19}F, ^{13}C). **Caution!** Even very small amounts of impurities lower the decomposition temperature of the isolated solid **2**. Crystallization was unsuccessful.

Compound **1** was obtained as the major product under analoguous conditions with a stoichiometry XeF_2:$Me_3SiC_6F_5$ = 1:1.

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Table 1. NMR spectroscopic data of selected pentafluorophenylxenon compounds.[a]

Compound	δ(F-2,6)	δ(F-3,5)	δ(F-4)	δ(Xe)	^3J(Xe,F)	δ(C-1)	^1J(Xe,C)	Solvent (*T* [°C])
$[C_6F_5Xe][B(C_6F_5)_2F_2]$[2b]	−125.2	−154.7	−142.0	−1980	69	82.8	119	MeCN/(−30)
*C_6F_5*$XeOCOC_6F_5$[b], [10]	−128.3	−154.8	−144.7	−2030	86	91.3	n.b.	CD_2Cl_2/(−10)
$[(C_6F_5Xe)_2Cl][AsF_6]$[9]	−128.6	−155.5	−144.3	−2116	81	92.9	195	CD_3CN/(−40)
C_6F_5XeF **1**	−129.3	−157.8	−148.4[c]	−2004	82			MeCN/(−30)
	−128.8	−156.1	−146.5[d]	−1994	80			CH_2Cl_2/(−30)
	−129.9	−158.1	−148.6[e]		81			EtCN/MeCN/(−58)
C_6F_5XeCl[9]	−130.8	−155.5	−146.2	−2295	94	101.6	208	CD_2Cl_2/(−60)
$Xe(C_6F_5)_2$ **2**	−131.4	−158.4	−153.4	−2376	45[f]	123.2[g]	320	$(CD_3)_2CO$/(−58)

[a] NMR spectra were recorded by using Bruker AMX 300 and AC 200 spectrometers. Chemical shifts were determined with respect to external XeF_2 (^{129}Xe), CCl_3F (^{19}F), and TMS (^{13}C). [b] $\delta(^{129}Xe)$ of $C_6F_5XeOCOC_6F_5$ calculated according to ref. [17]: $\delta(XeF_2) = \delta(XeF_4O) + 1822$. [c] $\delta = 4.5$ (tm, broad, $^1J(Xe,F) = 4099.6$ Hz; FXe). [d] $\delta = -1.6$ (tm, $^1J(Xe,F) = 4035.9$ Hz; FXe). [e] $\delta = 2.3$ (ψ-sept, $^1J(Xe,F) = 4125.0$ Hz; FXe). [f] $^4J(Xe,F) = 34.7$ Hz; $^5J(Xe,F) = 9.5$ Hz. [g] $^{13}C\{^{19}F\}$ NMR: $\delta = 143.4$ (s, $^2J(Xe,C) = 148$ Hz; C-2,6), 136.7 (s; C-3,5), 141.1 (s; C-4).

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C_6F_5XeF, A Key Substrate in Xenon–Carbon Chemistry: Synthesis of Symmetric and Asymmetric Pentafluorophenylxenon(II) Derivatives**

Hermann-Josef Frohn* and Michael Theißen

Salt-like compounds with a C–Xe bond in the cationic part $[RXe]^+$ have been known since 1989, where R represents an aryl,[1] alkenyl,[2] or alkynyl group[3]. In contrast $C_6F_5XeO_2CC_6F_5$,[4] C_6F_5XeCl and $[(C_6F_5Xe)_2Cl]^+$[5] contain weaker covalent C–Xe bonds (3c-4e bonds[6], asymmetric, hypervalent bonds with different distinct heteropolar components). The existence of the symmetric, hypervalent, molecular compound $Xe(CF_3)_2$[7] is extremely doubtful, and unambiguous proof of its constitution has not yet been provided.

On the basis of high values of group electronegativity, for example, $Xe(C_6F_5)_2$ and $Xe(CN)_2$ should be favored for a new class of symmetric C-Xe-C molecules, since their C(1) atom is part of a polarizable π system and the strongly electron-withdrawing components make the C-ligand electron-poor.

Herein we present a new concept for the synthesis of covalent C_6F_5Xe-C and C_6F_5Xe-Y compounds, specific examples being $Xe(C_6F_5)_2$ and C_6F_5XeCN[8]. This concept is based on the new molecule C_6F_5XeF (**1**)[9] which is the decisive key substrate. The asymmetric hypervalent molecule **1** is formed in 70 % yield as the soluble product of the heterogeneous low-temperature reaction of $[C_6F_5Xe]^+$ salts with "naked" fluoride $[NMe_4]F$ in CH_2Cl_2 [Eq. (1)]. The alternative approach, the electrophilic substitution of E in C_6F_5-E with $[FXe]^+$ does not lead to **1**, because the oxidation potential of $[FXe]^+$ is too high even for fluoroaromatics.

$$[C_6F_5Xe][Y]_{(s)} + [NMe_4]F \xrightarrow[\text{slow}]{CH_2Cl_2,\ -78\,^\circ C} \underset{\mathbf{1}}{C_6F_5XeF} + [NMe_4][Y]\downarrow \qquad (1)$$

$$Y = AsF_6,\ BF_4$$

If the soluble source of fluoride in Equation (1) is used in a smaller than stoichiometric amount, multinuclear fluoro-bridged xenonium species result [Eq. (2)]:

$$2\,[C_6F_5Xe][AsF_6]_{(s)} + [NMe_4]F \xrightarrow[\text{slow}]{CH_2Cl_2,\ -78\,^\circ C} [(C_6F_5Xe)_2F][AsF_6]\downarrow + [NMe_4][AsF_6]\downarrow \qquad (2)$$

Ab initio calculations (comparison in the gas phase) show that the C–Xe distance in **1** is longer than in the $[C_6F_5Xe]^+$ ion and the Xe–F distance is greater than in XeF_2. The latter feature makes the F^- ion a good leaving group. The permanent dipole moment in **1** makes the successful attack of nucleophiles on the electrophilic Xe center easier. With $Cd(C_6F_5)_2$ as an aryl transfer reagent it is possible to introduce a second aryl group into **1** [Eq. (3)]:

$$2\,\underset{\mathbf{1}}{C_6F_5XeF} + Cd(C_6F_5)_2 \xrightarrow[\text{fast}]{CH_2Cl_2,\ -78\,^\circ C} 2\,\underset{\mathbf{2}}{Xe(C_6F_5)_2} + CdF_2\downarrow \qquad (3)$$

The direct introduction of the C_6F_5 group into XeF_2 within the thermal-existence range of **2** is not successful with $Cd(C_6F_5)_2$, as the nucleophilicity of the aryl group (no permanent dipole moment) does not suffice for the substitution on XeF_2. The nucleophilicity of the aryl group in $Me_3SiC_6F_5$ in CH_2Cl_2 is not high enough for the successful F-C_6F_5 substitution in **1** [Eq. (4)] (see also ref. [10]):

$$C_6F_5XeF + Me_3SiC_6F_5 \not\xrightarrow[CH_2Cl_2,\ <10\,h]{-70\to-40\,^\circ C} \mathbf{2} + Me_3SiF \qquad (4)$$

However, with Me_3SiCN the CN group can be introduced successfully into **1** [Eq. (5)]:

$$\underset{\mathbf{1}}{C_6F_5XeF} + Me_3SiCN \xrightarrow[\text{spontaneous}]{CH_2Cl_2,\ -78\,^\circ C} \underset{\mathbf{3}}{C_6F_5XeCN} + Me_3SiF \qquad (5)$$

We attribute the different reactivities of $Me_3SiC_6F_5$ and Me_3SiCN more to differences in Lewis acidity than to steric effects.

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[*] Prof. Dr. H.-J. Frohn, Dipl.-Chem. M. Theißen
Fachgebiet Anorganische Chemie
Gerhard-Mercator-Universität Duisburg
Lotharstrasse 1, 47048 Duisburg (Germany)
Fax: (+49) 203-379-2231
E-mail: frohn@uni-duisburg.de

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