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BIS(α,β-DITRIFLOXYSTYRYL)MERCURY: SYNTHESIS AND CRYSTAL STRUCTURE

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Summary

Reaction of bis(α-diazophenacyl)mercury or its *p*-methyl derivative with triflic anhydride [$(CF_3SO_2)_2O$] leads to three diastereomeric bis(α,β-ditrifloxystyryl)mercury compounds. For (*E*,*E*)-bis(α,β-ditrifloxystyryl)mercury, an X-ray structural determination was carried out. The reaction represents another example of attack of the anhydride on the oxygen atom of an α-diazocarbonyl compound.

We recently reported that reaction of trifluoromethanesulfonic anhydride (triflic anhydride, Tf_2O) with azibenzils yields 1,2-vinylenebis(trifluoromethanesulfonates) [1]. The initial step of this reaction is an electrophilic attack of the anhydride on the oxygen atom of the diazocarbonyl unit. This is significant because α-diazocarbonyl compounds are ambident towards electrophiles and there are more examples of electrophilic attack at carbon than at oxygen. However, mercury-substituted α-diazocarbonyl compounds are sometimes used in electrophilic diazoalkane substitutions, and in such reactions only attack at carbon by the electrophilic species has been observed [2,3].

Thus, attack by Tf_2O at carbon in bis(α-diazophenacyl)mercury (**1a**) would yield the sulfonyl-substituted diazo compound (**2**) after displacement of the mercury residue. However, only the three diastereomeric divinylmercurials (*E*,*E*)-(**3a**), (*E*,*Z*)-(**3a**) and (*Z*,*Z*)-(**3a**) were obtained in a total yield of 22%; the rest was polymeric material. These compounds clearly arise from an initial attack of Tf_2O at oxygen in the diazo compound (see below). The tolyl compound (**1b**) reacts analogously, with a total yield of 21.5% for the three diastereomers of **3b**.

The assignment of configuration is only straightforward for the (*E*,*Z*)-isomers of **3a** and **3b**, both of which show two ^{19}F NMR signals in a 3/1 intensity ratio. As all four triflate groups of this isomer are chemically different, the signals of three of them must coincide accidentally. The ^1H NMR data also reveal the different configurations of the two vinyl groups (see Table 1). No distinction can be made, however, for the other two isomers, both of which are expected to give two ^{19}F signals of equal intensity (as Table 1 shows, these signals coincide in one di-

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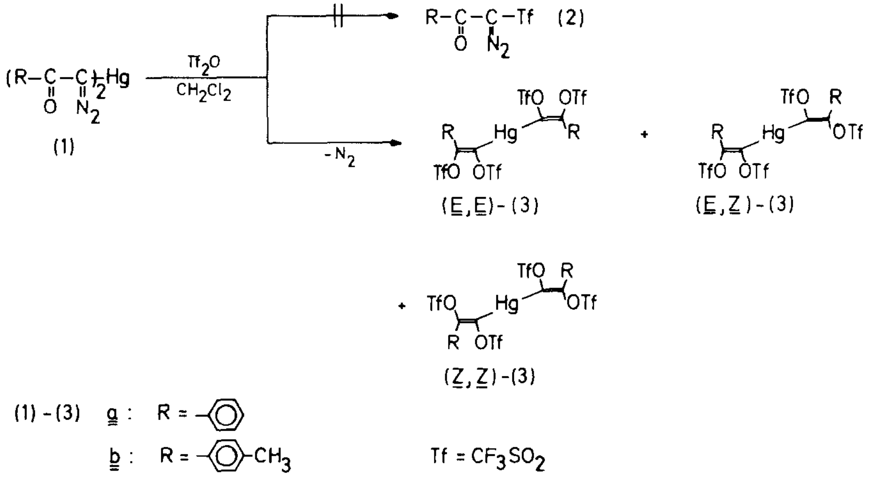

astereomer). Therefore an X-ray structure analysis of the major isomer of **3a** was carried out, and this clearly established its (*E*,*E*)-configuration.

The reaction involves initial formation of the alkenediazonium ion (**4**) *, the double-bond configuration of which depends on the preferred conformation around the C(O)–C(N_2) bond of **1**. Loss of N_2 from **4** gives the linear vinyl cation **5**. Preferential formation of the (*E*,*E*)-isomer of **3** can be explained in terms of either

TABLE 1

YIELDS AND SPECTROSCOPIC DATA OF COMPOUNDS 3

	Yield (%)	^{19}F NMR ^{a} δ(ppm)	^{1}H NMR δ(ppm)	IR (cm^{-1}, KBr pellet)
(*E*,*E*)-**3a**	13.5	88.3, 89.3 (1/1)	7.23–7.63 (m)	1640w, 1435s, 1250vs, 1220vs, 1146vs, 1040s, 1002s
(*E*,*Z*)-**3a**	7.9	88.3, 89.3 (1/3)	7.50 (s) 7.60 (m)	1624w, 1422vs, 1388s, 1223vs, 1212vs, 1132vs, 1032s, 1005s
(*Z*,*Z*)-**3a**	0.6	89.3	7.53 ("s")	1630w, 1425s, 1395s, 1262vs, 1221vs, 1128vs, 1100sh, 1032vs, 1015vs
(*E*,*E*)-**3b**	14	88.2, 89.2 (1/1)	2.46 (6H) 7.23 (s,8H)	1625w, 1603w, 1425vs, 1408s, 1238vs, 1207vs, 1138vs, 1128vs, 1046/1033/1022s, 992s
(*E*,*Z*)-**3b**	6.5	88.0, 89.2 (1/3)	2.40(3H), 2.43(3H) 7.13–7.63 (m,8H)	1628w, 1604w, 1417s, 1387s, 1248-1203vs, 1133s, 1121s, 1030s, 1002, 988s
(*Z*,*Z*)-**3b**	1	89.0	2.42 (s,6H) 7.10–7.60 (m,8H)	1630w, 1422s, 1258vs, 1232vs, 1148vs, 1036s, 1021s

[a] Solvent $CDCl_3$; values downfield from C_6F_6. [b] Solvent $CDCl_3$, TMS as standard.

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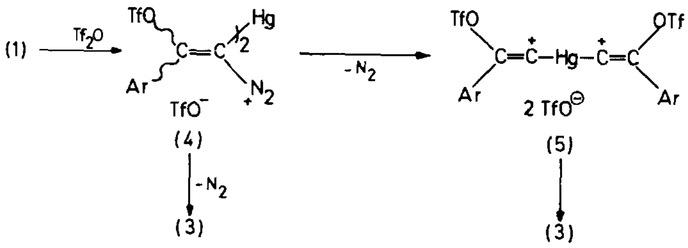
* For this discussion it does not matter whether the symmetrical intermediates **4** and **5** or unsymmetrical ones, produced by subsequent reaction at the two diazocarbonyl moieties of **1**, are assumed.

attack of a triflate anion from the less hindered side of **5**, or of an ion pair mechanism involving species **4**. These possibilities have been discussed before [1].



When bis(α-diazo-2,4,6-trimethylphenacyl)mercury or bis(1-diazo-3,3-dimethyl-2-oxobutyl)mercury were allowed to react with Tf_2O in the same manner as **1a** and **1b**, N_2 evolution was again observed. However, no compounds analogous to **3** nor any other products could be detected in significant amounts after workup. The reason for this is not clear.

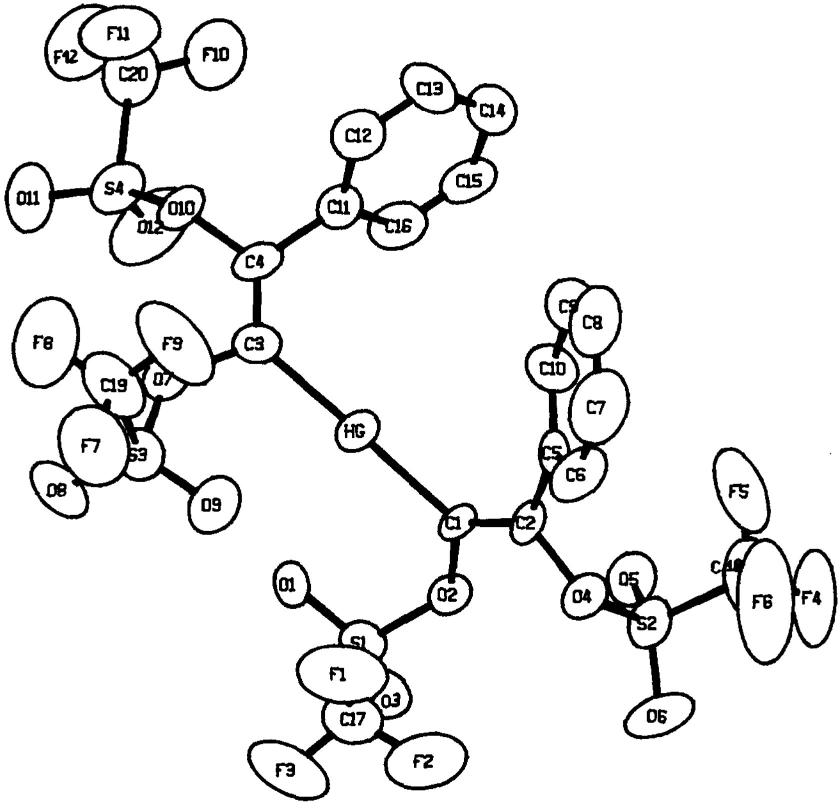


Fig. 1. ORTEP plot of (*E*,*E*)-**3a**. The size of the ellipsoids represents a 33% probability.

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) IN (*E*,*E*)-**3a**

Hg–C(1)	2.054(12)	Hg–C(3)	2.031(15)	*Mean values*			
C(1)–C(2)	1.276(15)	C(3)–C(4)	1.25(2)	C(17)–F	1.29(1)	C(19)–F	1.29(6)
C(1)–O(2)	1.447(13)	C(3)–O(7)	1.483(15)	C(18)–F	1.29(3)	C(20)–F	1.29(3)
C(2)–O(4)	1.424(13)	C(4)–O(10)	1.433(15)				
C(2)–C(5)	1.49(2)	C(4)–C(11)	1.51(2)				
S(1)–O(2)	1.547(9)	S(3)–O(7)	1.559(11)	S(2)–O(4)	1.554(9)	S(4)–O(10)	1.553(10)
S(1)–O(1)	1.395(8)	S(3)–O(8)	1.415(10)	S(2)–O(5)	1.373(9)	S(4)–O(11)	1.410(14)
S(1)–O(3)	1.397(9)	S(3)–O(9)	1.400(11)	S(2)–O(6)	1.422(10)	S(4)–O(12)	1.432(15)
S(1)–C(17)	1.82(2)	S(3)–C(19)	1.77(2)	S(2)–C(18)	1.80(2)	S(4)–C(20)	1.78(3)
C(1)–Hg–C(3)	177.9(6)						
Hg–C(1)–C(2)	127(1)	Hg–C(3)–C(4)	131(1)	O(1)–S(1)–O(2)	110.3(5)	O(7)–S(3)–O(8)	106.4(8)
Hg–C(1)–O(2)	118.1(8)	Hg–C(3)–O(7)	118(1)	O(2)–S(1)–O(3)	107.4(6)	O(7)–S(3)–O(9)	111.0(6)
O(2)–C(1)–C(2)	115(1)	O(7)–C(3)–C(4)	112(1)	O(1)–S(1)–O(3)	122.4(7)	O(8)–S(3)–O(9)	124.7(8)
C(1)–C(2)–O(4)	122(1)	C(3)–C(4)–O(10)	123(2)	O(2)–S(1)–C(17)	101.2(9)	O(7)–S(3)–C(19)	95(1)
C(1)–C(2)–C(5)	125(1)	C(3)–C(4)–C(11)	124(2)	O(1)–S(1)–C(17)	106.5(9)	O(8)–S(3)–C(19)	106.9(9)
O(4)–C(2)–C(5)	113(1)	O(10)–C(4)–C(11)	112(1)	O(3)–S(1)–C(17)	107(1)	O(9)–S(3)–C(19)	109(1)
C(1)–O(2)–S(1)	125.3(8)	C(3)–O(7)–S(3)	123.2(9)	O(4)–S(2)–O(5)	111.8(6)	O(10)–S(4)–O(11)	108.1(9)
C(2)–O(4)–S(2)	124.3(8)	C(4)–O(10)–S(4)	119.2(8)	O(4)–S(2)–O(6)	106.9(6)	O(10)–S(4)–O(12)	110.4(7)
				O(5)–S(2)–O(6)	122.7(7)	O(11)–S(4)–O(12)	124(1)
				O(4)–S(2)–C(18)	100(1)	O(10)–S(4)–C(20)	103(1)
				O(5)–S(2)–C(18)	107(1)	O(11)–S(4)–C(20)	105(1)
				O(6)–S(2)–C(18)	106(1)	O(12)–S(4)–C(20)	104(2)

Crystal structure of (*E*,*E*)-3a

Figure 1 shows the structure of the molecule. Bond lengths and bond angles are given in Table 2. The C(3)–Hg–C(1) connection is almost linear (177.9(6)°) and the average Hg–C bond length (2.04 ± 0.02 Å) is equal within the error limits to that found in another symmetrically substituted divinylmercurial [4]. A range of 2.00–2.10 Å seems to be usual for the Hg–C bond in alkyl-, vinyl- and phenyl-substituted mercurials [5].

The high amplitudes of thermal vibration, especially in the triflate groups, may be caused either by dynamic or static disorder. The anisotropy of the vibrations is probably not adequately described by the vibrational ellipsoid model, and systematic errors may be introduced in the refinement process. This prevents determination of a reliable bond geometry for these atoms. The mean values for the C–F bonds in the four CF_3 groups are the same, but as expected, much shorter (by 0.04 Å) than the bond lengths revealed by a low-temperature study of triflic acid monohydrate [6], where thermal motion, including torsional motion around the C–S bond, would be greatly reduced.

The two vinyl systems of the molecule are tilted against each other with an interplanar angle of 51.9° between the Hg–C(3)–C(4) and Hg–C(1)–C(2) planes. This situation is similar to di-*trans*-*β*-styrylmercury, where a value of 66.8° has been found [4]. Styryl conjugation must be only slight in the crystalline state. The phenyl rings are tilted by 51.1 and 51.8° relative to the respective Hg–C–C planes.

Experimental

^1H NMR spectra: Varian EM 390 (90 MHz). ^{19}F NMR spectra: Varian EM 390 (84.67 MHz). IR spectra: Perkin–Elmer model 397. Elemental analysis: Perkin–Elmer Elemental Analyzer 240. Silica gel for column chromatography was kept at 150°C/0.2 Torr for 6 h before use.

Preparation of bis(α-diazo-4-methylphenacyl)mercury (1b)

Powdered yellow HgO (2.22 g, 10 mmol) was added to a solution of 1-diazo-2-(4-tolyl)ethanone [7] (3.20 g, 20 mmol) in 30 ml of THF. The mixture was stirred for 3 d in the dark, then light petroleum ether (150 ml) was added. After filtration, the product was extracted with ethyl acetate. Evaporation of the solvent and trituration of the residue with petroleum ether gave 3.20 g (31%) of **1b** as a yellow powder, m.p. 126°C (dec.). IR(KBr): $\nu(CN_2)$ 2100 cm^{-1}. Anal. Found: C, 41.5; H, 2.76; N, 10.0. $C_{18}H_{14}HgN_4O_2$ calcd.: C, 41.6; H, 2.72; N, 10.8%.

When **1b** was prepared by the procedure used for **1a** [8], a yield of 22% was obtained.

Preparation of bis{α,β-bis[(trifluoromethanesulfonyl)oxy]styryl}mercury (3a)

A solution of 2.34 ml (14 mmol) of triflic anhydride [9] in 10 ml of dichloromethane was added dropwise to a suspension of **1a** [8] (3.44 g, 7 mmol) in 25 ml of dichloromethane at −20°C. The mixture was stirred for another 30 min at this temperature, then allowed to reach room temperature. When N_2 evolution had ceased, the solvent was removed in vacuo. Flash column chromatography (220 g of silica gel) with 2000 ml of dichloromethane/pentane (1/2 v/v) yielded:

(a) (*Z*,*Z*)-**3a**, 40 mg (0.6%); m.p. 71°C. Anal. Found: C, 25.1; H, 1.22.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS FOR (*E*,*E*)-**3a** ($B_{eq} = 4/3\ \Sigma_i \Sigma_j \beta_{ij} \cdot \boldsymbol{a}_i \cdot \boldsymbol{a}_j$)

Atom	x/a	y/b	z/c	B_{eq}(Å^2)	Atom	x/a	y/b	z/c	B_{eq}(Å^2)
Hg	0.38697(5)	0.48623(3)	0.12273(3)	5.02(1)	O(9)	0.443(1)	0.5399(6)	0.2209(4)	9.8(4)
S(1)	0.6252(3)	0.5669(2)	0.0874(2)	5.7(1)	O(10)	0.2806(9)	0.3297(5)	0.2228(4)	6.6(3)
S(2)	0.4184(4)	0.6459(2)	−0.0375(2)	6.3(1)	O(11)	0.385(1)	0.2698(7)	0.2846(6)	15.6(5)
S(3)	0.4564(4)	0.4854(3)	0.2528(2)	7.3(1)	O(12)	0.433(1)	0.2636(7)	0.1914(7)	15.7(6)
S(4)	0.3569(5)	0.2702(3)	0.2324(2)	10.1(2)	C(1)	0.413(1)	0.5582(6)	0.0692(5)	4.1(4)
F(1)	0.534(1)	0.6526(5)	0.1448(5)	13.5(4)	C(2)	0.342(1)	0.5942(7)	0.0475(5)	4.6(4)
F(2)	0.614(1)	0.6914(5)	0.0811(6)	14.6(5)	C(3)	0.361(1)	0.4177(8)	0.1777(6)	6.3(5)
F(3)	0.708(1)	0.6564(6)	0.1433(5)	14.4(4)	C(4)	0.297(1)	0.3697(7)	0.1785(6)	5.8(4)
F(4)	0.323(1)	0.6639(9)	−0.1220(4)	18.6(6)	C(5)	0.223(1)	0.5893(7)	0.0554(5)	4.4(4)
F(5)	0.2297(9)	0.6117(9)	−0.0660(5)	15.9(5)	C(6)	0.163(1)	0.6439(8)	0.0673(7)	8.0(5)
F(6)	0.251(1)	0.7125(7)	−0.0597(6)	22.8(5)	C(7)	0.054(1)	0.636(1)	0.0756(8)	10.5(6)
F(7)	0.351(1)	0.5399(8)	0.3223(5)	15.3(5)	C(8)	0.005(1)	0.576(1)	0.0729(8)	11.8(7)
F(8)	0.348(1)	0.438(1)	0.3275(5)	21.0(6)	C(9)	0.069(1)	0.524(1)	0.0607(7)	9.0(6)
F(9)	0.2534(9)	0.4847(8)	0.2746(4)	16.1(5)	C(10)	0.176(1)	0.5292(8)	0.0512(6)	6.6(5)
F(10)	0.224(1)	0.2019(6)	0.1783(5)	14.9(5)	C(11)	0.221(1)	0.3523(7)	0.1359(5)	5.4(4)
F(11)	0.183(1)	0.2102(7)	0.2539(6)	16.4(5)	C(12)	0.108(1)	0.3413(8)	0.1457(6)	7.0(5)
F(12)	0.312(1)	0.1484(6)	0.2332(6)	19.0(6)	C(13)	0.042(1)	0.3263(9)	0.1092(7)	8.3(6)
O(1)	0.6094(7)	0.5215(5)	0.1266(4)	6.1(2)	C(14)	0.075(2)	0.3252(9)	0.0594(7)	10.4(7)
O(2)	0.5237(7)	0.5701(5)	0.0527(4)	5.1(3)	C(15)	0.189(2)	0.3348(9)	0.0522(7)	8.7(6)
O(3)	0.7162(8)	0.5653(7)	0.0556(5)	8.8(4)	C(16)	0.257(1)	0.3468(8)	0.0784(6)	7.0(5)
O(4)	0.3718(7)	0.6498(4)	0.0176(4)	5.2(3)	C(17)	0.622(1)	0.6477(9)	0.1169(8)	9.4(6)
O(5)	0.451(1)	0.5834(5)	−0.0496(4)	6.7(3)	C(18)	0.297(2)	0.662(1)	−0.0734(8)	11.7(8)
O(6)	0.486(1)	0.7017(6)	−0.0442(5)	11.1(4)	C(19)	0.344(1)	0.481(1)	0.2948(7)	10.2(6)
O(7)	0.4299(8)	0.4204(5)	0.2239(4)	6.9(3)	C(20)	0.269(2)	0.202(1)	0.2247(8)	12.7(8)
O(8)	0.5503(9)	0.4728(7)	0.2824(5)	10.1(4)					

$C_{20}H_{10}F_{12}HgO_{12}S_4$ calcd.: C, 24.04; H, 1.01%.
(b) (*Z*,*E*)-**3a**, 550 mg (7.9%); m.p. 83°C. Anal. Found: C, 24.4; H, 1.01%.
(c) (*E*,*E*)-**3a**, 940 mg (13.5%); m.p. 77°C. Anal. Found: C, 24.2; H, 1.09%.

Preparation of bis{2-(4-tolyl)-1,2-bis[(trifluoromethanesulfonyl)oxy]vinyl}mercury (3b)

A solution of 1.4 ml (8.3 mmol) of triflic anhydride [9] in 5 ml of dichloromethane was added dropwise to a suspension of **1b** (2.16 g; 4.2 mmol) in 30 ml of dichloromethane at −30°C. After another 30 min the temperature was allowed to rise to room temperature. When N_2 evolution ceased the solvent was stripped off. Flash column chromatography of the residue (220 g silica gel; 2000 ml dichloromethane/pentane (1/2.5 v/v)) gave:
(a) (*Z*,*Z*)-**3b**, 45 mg (1%); m.p. 49°C. Anal. Found: C, 26.2; H, 1.40. $C_{22}H_{14}F_{12}HgO_{12}S_4$ calcd.: C, 25.7; H, 1.37%.
(b) (*Z*,*E*)-**3b**, 280 mg (6.5%); m.p. 74°C. Anal. Found: C, 26.1; H, 1.43%.
(c) (*E*,*E*)-**3b**, 600 mg (14%); m.p. 95°C. Anal. Found: C, 25.9; H, 1.38%.

X-Ray structure determination of (E,E)-3a

Crystal data. $C_{20}H_{10}F_{12}HgO_{12}S_4$, $M_r = 999.1$, orthorhombic, space group *Pbca*; a 12.312(4), b 20.364(6), c 26.192(4) Å, V 6567(5) Å^3, $Z = 8$, D_c 2.02 g cm^{-3}, μ(Mo-$K_{\bar{\alpha}}$) 49.2 cm^{-1}.

Data collection. Crystals were obtained by solvent evaporation from a solution in light petroleum ether. A crystal fragment with maximum dimensions 0.65 × 0.35 × 0.15 mm was used. Enraf–Nonius CAD 4 diffractometer, monochromatized Mo-K_α radiation, scan width $(0.85 + 0.35 \tan \theta)°$, scan speed 1.5–5° min^{-1}. An asymmetric unit with $0.049 \leqslant \sin \theta/\lambda \leqslant 0.550$ was explored (4608 reflections). Three monitoring reflections showed an intensity loss of 16.9% on the average, and the data set was corrected accordingly assuming linear decay. An empirical absorption correction (ψ scans) was applied (min. transmission 62.9%; max. transmission 98.1%).

Structure solution and refinement [10]. The Hg atom was located from a Patterson synthesis and the remainder of the molecule by Fourier methods. Hydrogen atom positions were calculated and included in the structure factor calculation with B 7.0 Å^2. Full-matrix least-squares refinement (2624 reflections with $I > 2\sigma(I)$; weighting scheme $w = [\sigma^2(F_0) + (0.03F_0)^2]^{-1}$; 442 variables) converged at $R = 0.069$, $R_w = 0.053$; $(\Delta/\sigma)_{max} = 0.62$. Final parameters for non-hydrogen atoms are given in Table 3 *.

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* Additional data (anisotropic thermal parameters, full list of bond distances and angles, structure factor tables) are available from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2. Requests should give deposition number CSD51172, the names of the authors and the literature citation.

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