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4-Acetyl-*trans*-3-methylcarbamoyl-1,4-thiazinane 1-Oxide

BY F. VANHOUTEGHEM, A. T. H. LENSTRA AND H. J. GEISE*

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

AND C. VAN DER AUWERA AND M. J. ANTEUNIS

State University of Gent, Laboratory of Organic Chemistry, Krijgslaan 281 – *S*4, *B*-9000 *Gent, Belgium*

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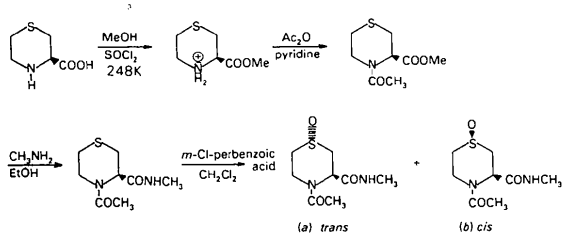
Abstract. $C_8H_{14}N_2O_3S$, $M_r = 218{\cdot}3$, monoclinic, $P2_1/n$, $a = 10{\cdot}363$ (6), $b = 12{\cdot}613$ (8), $c = 8{\cdot}307$ (5) Å, $\beta = 97{\cdot}95$ (3)°, $V = 1075$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}348$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}284$ mm^{-1}, $F(000) = 464$, room temperature, $R = 0{\cdot}038$ for 2033 independent observed reflections. The six-membered thiazinane ring adopts a distorted chair conformation with the methylcarbamoyl group in axial and the S=O and *N*-acetyl groups in inclinal position. The molecule contains a dipeptide fragment, whose geometry closely resembles that calculated for conformation IV of *N*-acetyl-*N'*-methylglycine amide. Comparison of the calculated values with the experimental ones of the title compound and its equivalent with axial S=O reveals differences inside the dipeptide fragment in seemingly equivalent bond lengths and angles. The synthesis and physico-chemical data are also reported.

Introduction. The title compound and its corresponding *cis*-3-methylcarbamoyl isomer were synthesized in a series of reactions presented below.



Our interest in these molecules is related to their peptide moiety consisting of C(6)O(2)C(5)N(1)C(3)-C(7)O(3)N(2)C(8) (Fig. 1). We asked ourselves to what extent the torsion angles in the backbone of the peptide fragment are affected when it is part of the six-membered thiazinane ring, upon which different strains are imposed.

Experimental. 1,4-Thiazinane-3-carboxylic acid (Carson & Wong, 1964) was esterified by treating a suspension in methanol at 248 K with 1·5 equivalent $SOCl_2$ for 1 h. The solution was kept at room temperature overnight, evaporated and the residue crystallized from methanol:hexane (1:3), giving the ester chlorohydrate in 79% yield. M.p. 446 K (dec.); $[\alpha]_D^{20.0°C} = -24{\cdot}8°$ [EtOH, 2·0 g dm^{-3}]; $R_f = 0{\cdot}58$ (TLC; $CHCl_3$:MeOH = 9:1).

4-Acetyl-3-methoxycarbonyl-1,4-thiazinane

1·9 ml (20 mmol) acetic anhydride was added to a solution of 17 mmol of the foregoing ester in 110 ml dry pyridine and the resulting yellowish solution was evaporated after 24 h standing at room temperature. The residue was twice evaporated after the addition of 50 ml toluene. 4-Acetyl-3-methoxycarbonyl-1,4-thiazinane was obtained with 97% yield as an oil, which could not be crystallized. $[\alpha]_D^{18·0°C} = -122{\cdot}3°$ [$CHCl_3$, 0·9 g dm^{-3}]; $R_f = 0{\cdot}72$ (TLC; $CHCl_3$:MeOH = 9:1). The ^{1}H NMR spectrum ($CDCl_3$, from TMS internal standard) reveals *cis:trans* isomerism about the acetamide bond (18% *cis*): 5·76 [H(3),*t*]; 4·97 [H(5)eq,*c*]; 4·75 [H(3),*c*]; 4·00 [H(5)eq,*t*]; 3·83 (OCH_3,*c*); 3·78 (OCH_3,*t*); 3·62 [H(5)ax,*t*]; 3·16 [H(2)eq,*c*]; 3·13 [H(2)eq,*t*]; 2·98 [H(5)ax,*c*]; 2·92 [H(2)ax,*c*]; 2·88 [H(2)ax,*t*]; 2·74 [H(6)ax,*t*]; 2·69 [H(6)ax,*c*]; 2·49 [H(6)eq,*t*]; 2·48 [H(6)eq,*c*]; 2·17 (CH_3CO,*t*); 2·07 (CH_3CO,*c*).

4-Acetyl-3-methylcarbamoyl-1,4-thiazinane

15 mmol of the foregoing 3-methoxycarbonyl compound was treated with 15 ml methylamine in 50 ml methanol for 31 h at room temperature. The reaction mixture was evaporated and the resulting oil crystallized from 30 ml 2-propanol containing a few drops of methanol. Yield: 98%, m.p. *ca* 371 K (dec.); $[\alpha]_D^{18·0°C} = -87{\cdot}0°$ [$CHCl_3$, 0·4 g dm^{-3}], see, however, below; $R_f = 0{\cdot}8$ (TLC; $CHCl_3$:MeOH = 4:1). The ^{1}H NMR spectrum ($CDCl_3$; TMS) reveals that 34% of the *cis*-acetamide isomer is present. A VPC analysis on a chiral stationary phase [Chirasil Val III (Alltech), 50 m, 393 K 8 min, 3° min^{-1} to 463 K] shows the presence of 23% of the D enantiomer, although the synthesis of 1,4-thiazinane-3-carboxylic acid was started from pure

* Author to whom correspondence should be addressed.

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L-cystine. This confirms the enantiomeric instability under basic conditions of the 4-acetyl derivatives, as expected.

4-Acetyl-3-methylcarbamoyl-1,4-thiazinane 1-oxide (cis and trans isomers)

2·5 g *m*-chloroperbenzoic acid was added to 12·4 mmol of 4-acetyl-3-methylcarbamoyl-1,4-thiazinane in 100 ml methylene chloride at 253 K. After 20 min the solution was extracted with 3 × 50 ml water and the combined water layers evaporated. The solid residue (foam) was shown by ^{1}H NMR to consist of 61% *trans*-oxide and 39% *cis*-oxide. The mixture was separated by column chromatography (silica gel, gradient elution from $CHCl_3$ to 60% MeOH) to give 1·55 g of the *trans*- and 0·85 g of the more polar *cis*-sulfoxide isomer. Total yield 90%. Although both fractions show optical activity they may contain appreciable amounts of the racemic modifications. A well formed crystal of the *cis* isomer was grown from $CHCl_3$, and happened to be enantio pure as was demonstrated by X-ray analysis (Sanni, De Wolf, Lenstra, Van der Auwera & Anteunis, 1984). Well formed crystals of the *trans* isomer were obtained by very slow evaporation of highly concentrated $CHCl_3$ solution, next to small needles and an oily fraction. The well grown crystals – suitable for an X-ray determination, to be reported here – were washed with cold $CHCl_3$ and ether. They turned out to be a racemic mixture. Racemic *trans* isomer (*a*): m.p. 434 K (dec.); $R_f = 0·31$ ($CHCl_3$:MeOH=4:1). ^{1}H NMR ($CDCl_3$) at 253 K revealed *cis/trans*-acetamide isomers in the ratio 8/92; 6·83 (NH, *c* + *t*); 5·56 [H(3),*t*]; 4·95 [H(5)eq,*c*]; 4·90 [H(3),*c*]; 4·11 [H(5)eq,*t*]; 3·92 [H(2)eq,*t*]; 3·64 [H(5)ax,*t*]; 3·43 [H(6)eq,*t*]; 3·37 [H(6)eq,*c*]; 2·87 (NMe,*c*); 2·80 (NMe,*t*); 2·77 [H(6)ax,*c*]; 2·65 [H(2)ax,*t*]; 2·30 (CH_3CO,*t*); 2·24 (CH_3CO,*c*). L-*cis* isomer (*b*): m.p. 461 K; $R_f = 0·22$ ($CHCl_3$:MeOH = 4:1). ^{1}H NMR ($CDCl_3$:d_6-Me_2SO = 8:2) showed *cis/trans*-acetamide isomers in the ratio 30/70; 7·92 (NH,*c*); 7·00 (NH,*t*); 5·58 [H(3),*t*]; 4·84 [H(5)eq,*c*]; 4·75 [H(3),*c*]; 4·35 [H(5)ax,*t*]; 3·96 [H(5)eq,*t*]; 3·84 [H(2)eq,*t*]; 3·79 [H(2)eq,*c*]; 3·61 [H(5)ax,*c*]; 2·91 [H(6)eq,*t*]; 2·85 (NMe,*t*); 2·83 (NMe,*c*); 2·69 [H(6)ax,*t*]; 2·58 [H(2)ax,*t*]; 2·27 (CH_3CO,*t*); 2·24 (CH_3CO,*c*).

Unit-cell dimensions determined from 25 high-order reflections. Intensity data collected up to a glancing angle $\theta = 27°$ ($0 \le h \le 13$; $0 \le k \le 16$; $-10 \le l \le 10$) in ω/θ scan mode; Mo radiation, graphite monochromator. Three intensity-control reflections measured every 2 h showed no crystal decay. Enraf–Nonius CAD-4 diffractometer. Crystal 0·15 × 0·15 × 0·2 mm. No absorption correction. 2338 independent reflections, 2033 considered observed with $I > 2\sigma(I)$. The Patterson vector map gave the S position and a Fourier map, calculated on the S phases, revealed remaining non-H atoms. After a few cycles of least-squares refinement (on *F*) (Enraf–Nonius *Structure Determination Package,* Frenz, 1978), a difference electron density map showed positions of all H atoms. All positional parameters refined with anisotropic temperature parameters for non-H atoms and one isotropic temperature factor $B = 4$ Å^2 for H atoms (overall *B* in Wilson plot 3 Å^2), 170 variables. Reflections weighted individually with a weight based on counting statistics. Refinement of the extinction correction to $1·30 \times 10^{-6}$ mm (Zachariasen, 1963) resulted in $R = 0·038$, $wR = 0·042$, $S = 4·84$ with $(\Delta/\sigma)_{max} = 0·09$. Max. peak in final difference Fourier map 0·15 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. It follows from the space group ($P2_1/n$) that the crystal used in the analysis consisted of a racemic mixture. Final values of the refined parameters are summarized in Table 1,* while the numbering scheme of the atoms is given in Fig. 1. Fig. 1 and Table 1 give the molecule in the (3*S*)-configuration. However, to facilitate the comparison with similar molecules, we give in what follows the geometrical parameters of the (3*R*)-configuration.

CH distances range from 0·79 to 1·01 Å with an average of 0·96 Å; other bond lengths, valence angles and a selection of torsion angles are given in Table 2. It follows from the sign distribution of endocyclic torsion angles that the six-membered ring has a chair conformation. Cremer & Pople (1975) ring parameters of the (3*R*)-configuration, with e.s.d.'s according to Norrestam (1981), are: $q_2 = 0·143$ (7), $q_3 = -0·636$ (7), $Q = 0·652$ (7) Å, $\varphi_2 = 200$ (3), $\theta_2 = 167$ (1)° for the sequence S,C(1),C(2),N(1),C(3),C(4). The experimental values point to a distortion of the chair, although the amount of distortion is difficult to assess, because exact standard Cremer & Pople values and torsion angles are not known for this type of ring (Petit, Dillen & Geise, 1983). The angle (α) between an exocyclic valency and the plane of the ring (Cremer & Pople, 1975) is a useful measure to define the orientation of a substituent. A substituent is considered in equatorial position when $0 \le |\alpha| \le 30°$, in inclinal position when $30 < |\alpha| \le 60°$ and in axial position when $60 < |\alpha| \le 90°$. Polar angles α of S=O [α = 44·0 (4)°], N(1)–C(5) [α = 32·1 (4)°] and C(3)–C(7) [α = 75·6 (4)°] show that the methylcarbamoyl substituent is in axial position, whereas the orientation of the S=O and of the acetyl group is inclinal.

* Lists of H positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42457 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A detailed comparison of the geometrical parameters of the title compound with those (Table 2) of 4-acetyl-*cis*-3-methylcarbamoyl-1,4-thiazinane 1-oxide (Sanni *et al.*, 1984) – which differs only in the orientation (axial) of the S=O group – reveals many interesting differences and similarities. The axial S=O group in the *cis* derivative pushes O(3) away, which rationalizes the differences in the torsion angles around C(3)–C(7) between the *cis* and the *trans* (title) compound. Furthermore, the six-membered ring of the title compound is decidedly more puckered, particularly at the substituted side C(3), C(4) and N(1). In keeping with the increased puckering we note a decrease in the valence angles N(1)–C(3)–C(4), S–C(4)–C(3) and S–C(1)–C(2). Apart from the exocyclic valence angle N(1)–C(3)–C(7), which is smaller in the *trans* derivative, other details of both compounds show a close correspondence.

The most interesting aspect of the two molecules concerns the fragment consisting of C(6)O(2)C(5)-N(1)C(3)C(7)O(3)N(2)C(8). The fragment constitutes a dipeptide in the α-helical conformation (Lewis,

Table 1. *Positional parameters in fractions of the cell edges and isotropic temperature parameters* (Å²)

The e.s.d.'s given in parentheses refer to the last significant digit. Isotropic temperature factors are calculated from the anisotropic temperature parameters assuming equal volume of the 50% probability region. B_{iso} was calculated according to Lipson & Cochran (1968): $B_{iso} = 8\pi^2(U^o_{11}U^o_{22}U^o_{33})^{1/3}$. All anisotropic thermal parameters were physically acceptable.

	x	*y*	*z*	B_{iso}
S	0·52521 (4)	0·35246 (4)	0·39981 (6)	2·95
O(1)	0·6091 (1)	0·4037 (1)	0·5408 (2)	3·90
O(2)	0·3241 (1)	−0·0225 (1)	0·3842 (2)	4·37
O(3)	0·5954 (1)	0·1729 (1)	0·0943 (2)	4·76
N(1)	0·3393 (1)	0·1530 (1)	0·3458 (2)	2·45
N(2)	0·3857 (2)	0·1274 (1)	0·0258 (2)	3·67
C(1)	0·3640 (2)	0·3370 (1)	0·4523 (2)	3·07
C(2)	0·2865 (2)	0·2610 (1)	0·3342 (2)	2·70
C(3)	0·4729 (2)	0·1414 (1)	0·3123 (2)	2·56
C(4)	0·5661 (2)	0·2136 (1)	0·4185 (2)	3·04
C(5)	0·2744 (2)	0·0654 (2)	0·3868 (2)	3·12
C(6)	0·1411 (2)	0·0789 (2)	0·4342 (3)	4·26
C(7)	0·4893 (2)	0·1503 (1)	0·1320 (2)	3·11
C(8)	0·3912 (3)	0·1254 (2)	−0·1474 (3)	5·26

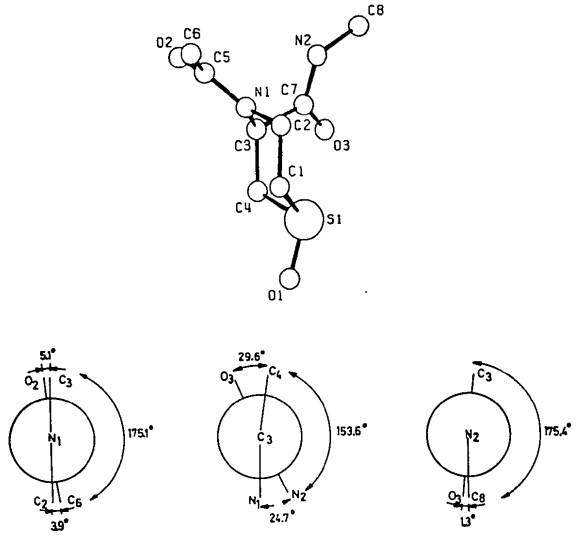

Fig. 1. Structural formula, conformation and numbering scheme of atoms of the title compound. Newman projections along C(5)–N(1), C(7)–C(3) and N(2)–C(7) show the arrangement of the substituents (e.s.d.'s about 0·3°). Note that the (3*S*)-configuration is shown.

Table 2. *Bond lengths* (Å), *valence and selected torsion angles* (°) *with e.s.d.'s in parentheses*

The first column contains the values of the title compound, the second those of 4-acetyl-*cis*-3-methylcarbamoyl-1,4-thiazinane 1-oxide (Sanni *et al.*, 1984), and the third those calculated for conformation IV of *N*-acetyl-*N'*-methylglycine amide (Schäfer *et al.*, 1982).

	trans	*cis*	Calc.
S=O(1)	1·504 (2)	1·495 (1)	
S–C(1)	1·795 (2)	1·792 (2)	
S–C(4)	1·804 (2)	1·817 (2)	
N(1)–C(2)	1·466 (2)	1·480 (2)	
N(1)–C(3)	1·457 (2)	1·451 (2)	1·458
N(1)–C(5)	1·362 (2)	1·344 (2)	1·372
N(2)–C(7)	1·323 (2)	1·313 (2)	1·347
N(2)–C(8)	1·449 (2)	1·456 (2)	1·462
C(1)–C(2)	1·520 (2)	1·494 (2)	
C(3)–C(4)	1·518 (2)	1·520 (2)	
C(3)–C(7)	1·535 (2)	1·529 (2)	1·531
C(5)–C(6)	1·498 (2)	1·485 (2)	1·517
C(5)–O(2)	1·223 (2)	1·242 (2)	1·217
C(7)–O(3)	1·218 (2)	1·219 (2)	1·223
O(1)–S–C(1)	108·3 (1)	106·2 (1)	
O(1)–S–C(4)	104·3 (1)	106·6 (1)	
C(1)–S–C(4)	95·1 (1)	94·6 (1)	
C(2)–N(1)–C(3)	115·9 (1)	117·0 (1)	
C(2)–N(1)–C(5)	125·3 (1)	123·8 (1)	
C(3)–N(1)–C(5)	118·8 (1)	119·2 (1)	119·8
C(7)–N(2)–C(8)	121·7 (1)	123·0 (1)	121·3
S–C(1)–C(2)	109·7 (1)	112·3 (1)	
N(1)–C(2)–C(1)	112·6 (1)	111·1 (1)	
N(1)–C(3)–C(4)	111·9 (1)	113·7 (1)	
N(1)–C(3)–C(7)	111·5 (1)	115·3 (1)	115·2
C(4)–C(3)–C(7)	112·1 (1)	113·1 (1)	
S–C(4)–C(3)	114·2 (1)	115·8 (1)	
N(1)–C(5)–C(6)	118·6 (1)	120·2 (1)	114·8
N(1)–C(5)–O(2)	120·4 (1)	120·5 (1)	121·6
C(6)–C(5)–O(2)	120·9 (1)	119·3 (1)	123·6
O(3)–C(7)–N(2)	123·9 (1)	124·1 (2)	124·3
O(3)–C(7)–C(3)	119·6 (1)	118·4 (1)	119·4
N(2)–C(7)–C(3)	116·4 (1)	117·4 (1)	116·2
C(4)–S–C(1)–C(2)	58·5 (3)*	58·5 (4)	
S–C(1)–C(2)–N(1)	−65·2 (3)	−66·4 (4)	
C(1)–C(2)–N(1)–C(3)	60·2 (3)	58·9 (4)	
C(2)–N(1)–C(3)–C(4)	−54·8 (3)	−51·2 (4)	
N(1)–C(3)–C(4)–S	57·7 (3)	52·0 (4)	
C(3)–C(4)–S–C(1)	−56·7 (3)	−51·7 (4)	
N(2)–C(7)–C(3)–C(4)	−153·6 (3)	−218·8 (4)	
C(3)–C(7)–N(2)–C(8)	175·4 (3)	171·5 (5)	179·2
C(6)–C(5)–N(1)–C(2)	3·9 (3)	−1·5 (5)	
C(5)–N(1)–C(3)–C(7)(φ)	−108·1 (3)	−98·2 (4)	−86·6
N(1)–C(3)–C(7)–N(2)(ψ)	24·7 (3)	7·9 (4)	14·2
C(6)–C(5)–N(1)–C(3)(ω)	−175·1 (3)	−178·3 (4)	−174·4

* The signs refer to the (3*R*)-configuration.

Momany & Scheraga, 1973) and closely resembles conformation IV of *N*-acetyl-*N'*-methylglycine amide for which an unconstrained *ab initio* geometry on the 4-21G level is published (Schäfer, Van Alsenoy & Scarsdale, 1982). The comparison (Table 2) between our experimental results and the calculated structure is remarkably good, keeping in mind the inherent distinction between X-ray and 4-21G *ab initio* distances. It reveals the existence of differences in primary parameters (bond distances and angles) that might have gone unnoticed and are, indeed, often neglected in standard geometries frequently used in peptide stereochemistry. For example the peptide N(2)–C(7) bond is about 0·03 Å shorter than the peptide N(1)–C(5) bond, while C(3)–C(7), *i.e.* the C–C(=O) inside the backbone, is about 0·04 Å longer than C(5)–C(6), *i.e.* the terminating C–C(=O). These observations, which are in agreement with the calculations, suggest a larger contribution from charged resonances of the type $^{\ominus}$O–C=N$^{\oplus}$–C to the structure of the *N'*-methyl amide side in comparison with the *N*-acetyl side. Furthermore, valence angles for which the experimental value is over 120° are matched, with only one exception, by calculated values larger than 120°. The same holds for angles under 120°. It shows that the large value (~124°) for O(3)–C(7)–N(2) is inherent to the *N'*-methylglycine amide fragment. The fact that the latter is part of a ring system explains the deviation of the C(5)–N(1)–C(3)–C(7) torsion angle from the calculated value. This, together with the aforementioned differences of the N(1)–C(3)–C(7) valence and the C(3)–C(7) torsion angles between the *cis* and *trans* derivatives, shows that the backbone of a peptide can be chemically manipulated to a certain extent.

Aside from this conclusion, the internal consistency of the experimental values and, moreover, the excellent agreement with the calculations, precisely at points where conformationally induced geometry variations were expected, strongly underline the conclusion of Schäfer *et al.* (1982) about the importance of local geometries for peptide conformations.

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Structure of the 3^1_{10}-Helical Pentapeptide Boc-L-Pro-Aib-L-Ala-Aib-L-Ala-OH

BY ROLAND BOSCH, GÜNTHER JUNG,* HERIBERT SCHMITT AND WERNER WINTER*†

Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, *D*-7400 *Tübingen* 1, *Federal Republic of Germany*

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Abstract. $C_{24}H_{41}N_5O_8$, $M_r = 527{\cdot}62$, orthorhombic, $P2_12_12$, $a = 18{\cdot}839$ (3), $b = 18{\cdot}776$ (7), $c = 9{\cdot}179$ (1) Å, $V = 3247{\cdot}0$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}079$ Mg m^{-3} (disordered hydrocarbon solvent not included), λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}601$ mm^{-1}, $F(000) = 1136$, $T = 293$ K, final $R = 0{\cdot}056$ for 2429 unique observed reflections. The pentapeptide (1) represents the N-terminal sequence 2–6 of the membrane-modifying icosapeptide antibiotic alamethicin F30. Pentapeptide (1) adopts a left-handed 3^1_{10}-helical structure of one type II followed by two type III consecutive β-turns with 4→1 hydrogen bonds. Despite

* To whom correspondence should be addressed.

† Present address: Forschungszentrum der Grünenthal GmbH, Zieglerstrasse 6, D-5100 Aachen, Federal Republic of Germany.

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