A Novel Dimerization Mode of a Cyclic Ketene Imine**

Elke Langhals, Rolf Huisgen,* and Kurt Polborn[a]

Dedicated to Mieczyslaw Makosza on the occasion of his 70th birthday

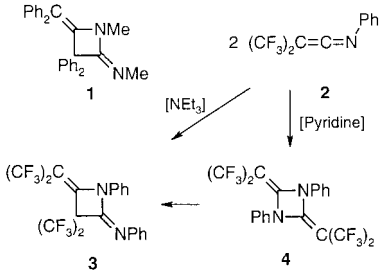
Abstract: The strained seven-membered cyclic ketene imine **9**, obtained by cycloaddition of thiocarbonyl ylide **6** with 2,3-bis(trifluoromethyl)fumaronitrile (**7**), underwent base-catalyzed dimerization at room temperature on treatment with KCN in acetonitrile or with proton sponge in acetonitrile or $CDCl_3$. Two diastereoisomeric dimers, (6*SR*,3′*RS*)-**13** and (6*SR*,3′*SR*)-**13**, were formed in 1:1 ratio in high yield. X-ray analysis revealed a deep-seated structural change which is unrelated to known dimerization pathways of ketene imines. In **13**, one of the seven-membered rings is opened, and attached to the second unit by a thioimidate group. An ionic chain reaction with a formal fluoride ion as transfer agent offers a rationalization.

Keywords: base catalysis · cycloaddition · dimerization · heterocycles · ketene imines

Introduction

Ketene imines rank below ketenes in their propensity to dimerize. Whereas dialkylketene *N*-methylimines slowly oligomerize at room temperature,[1] diphenylketene *N*-methylimine dimerizes on heating (125 °C, six weeks) to give the methyleneazetidine **1**;[2] the reaction corresponds to the spontaneous dimerization of ketene which affords 3-methyleneapropanolide. According to Gambaryan, bis(trifluoromethyl)ketene *N*-phenylimine (**2**) is far more electrophilic than unfluorinated ketene imines.[3] Although thermostable up to 150 °C, **2** is converted to **3**, that is, the unsymmetrical type of dimer, by catalysis with triethylamine at 20 °C.[4] In pyridine, **2** affords the *sym*-dimer **4** which is less stable, as shown by the subsequent conversion **4** → **3** (Scheme 1).[4–6]

Cyclic seven-membered ketene imines became available by two-step cycloadditions of thiocarbonyl ylides which are sterically hindered at one terminus, with 2,3-bis(trifluoromethyl)fumaronitrile (**7**).[7,8] When 1,1,3,3-tetramethylindan-2-thione *S*-methylide (**6**) is set free from the dihydro-1,3,4-thiadiazole (**5**) in the presence of **7**, the spirocyclic ketene imine **9** is formed nearly completely (Scheme 2).[9] The cumulated double bond system creates high strain in the seven-membered ring of **9**; the X-ray analysis revealed angle deformations.[7]



Scheme 1. Dimerization of open-chain ketene imines.

Storable in the crystalline state, **9** is converted in CD_3CN solution—slowly even at room temperature—to the spirothiolane **11**, the cyclopropane **10** (+thione), and compound **12** in parallel reactions. At 80 °C, spirothiolane **11** likewise disappears in favor of **10** and **12**.[9] The variety of reactions was interpreted by assuming the 1,5-zwitterion **8** as an intermediate. The switching from the concerted to the stepwise pathway of cycloaddition occurs when 1,3-dipole and dipolarophile drastically differ in nucleophilic and electrophilic character (review: ref. [10]).

Results and Discussion

A few crystals of KCN initiated the fading of the yellow solution of **9** in acetonitrile, and soon colorless crystals precipitated; after 15 min at room temperature, **13** was obtained in 89 % yield. Elemental analyses and determination of the

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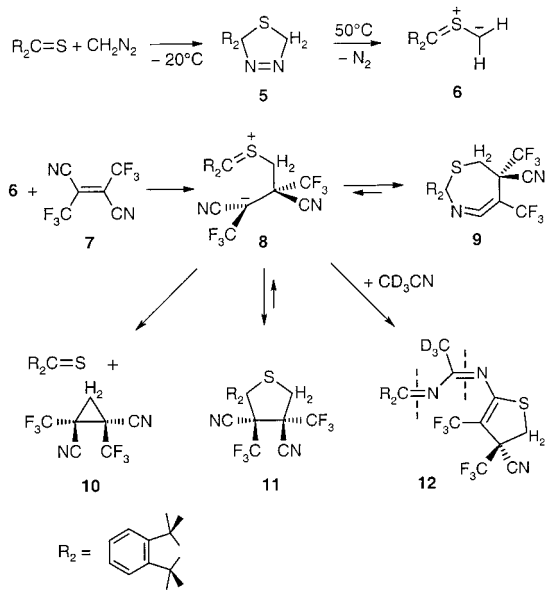


Scheme 2. Formation and reactions of the strained cyclic seven-membered ketene imine **9**.

molecular mass established a dimer, and the ^{19}F NMR spectrum revealed two diastereoisomers in nearly 1:1 ratio. Ten mol% of 1,8-bis(dimethylamino)naphthalene (proton sponge) in acetonitrile or—somewhat slower—in $CDCl_3$ likewise induced dimerization of **9**. The separation of the diastereoisomers was achieved by fractional crystallization: **13A** was isolated pure, and **13B** was enriched to 85%.

The X-ray diffraction pattern of **13A** disclosed a structure which showed no relation to the known types **3** and **4** of ketene imine dimers. Obviously, the ring strain is essential for the different course of dimerization.

The compact structure of **13A** was dissected in Figure 1 into a Northern and Southern hemisphere to allow closer inspection. The first contains one F-atom less than **9**, and the second one more. In the Northern part the hydro-1,3-thiazepine ring is preserved, whereas the ring-opened Southern part is attached to the 4-position of the Northern by a thioether function, thus generating a thioimidate structure.

Abstract in German: *Das 7-gliedrige cyclische Ketenimin **9**, das durch Cycloaddition des 1,1,3,3-Tetramethylindan-2-thion-S-methylids (**6**) mit 2,3-Bis(trifluormethyl)fumarnitril (**7**) erhalten wurde, trat bei Raumtemperatur in eine Basenkatalysierte Dimerisierung ein; Katalysatoren waren KCN in Acetonitril sowie Protonenschwamm in Acetonitril oder $CHCl_3$. Zwei diastereomere Dimere, (6SR,3′RS)-**13** und (6SR,3′SR)-**13** (~50:50), wurden in hoher Ausbeute gebildet. Die Röntgenstrukturanalyse lehrte, daß nur einer der siebengliedrigen Ringe erhalten blieb; aus dem des zweiten Moleküls ging ein 2-Azabutadien-System hervor, und ein Imidsäure-thioester bietet die Verknüpfung. Es gibt keine Beziehung zu den bekannten Wegen der Ketenimin-Dimerisierung. Als Mechanismus der Dimerisierung wird eine ionische Kettenreaktion mit Fluorid-Übertragung vorgeschlagen.*

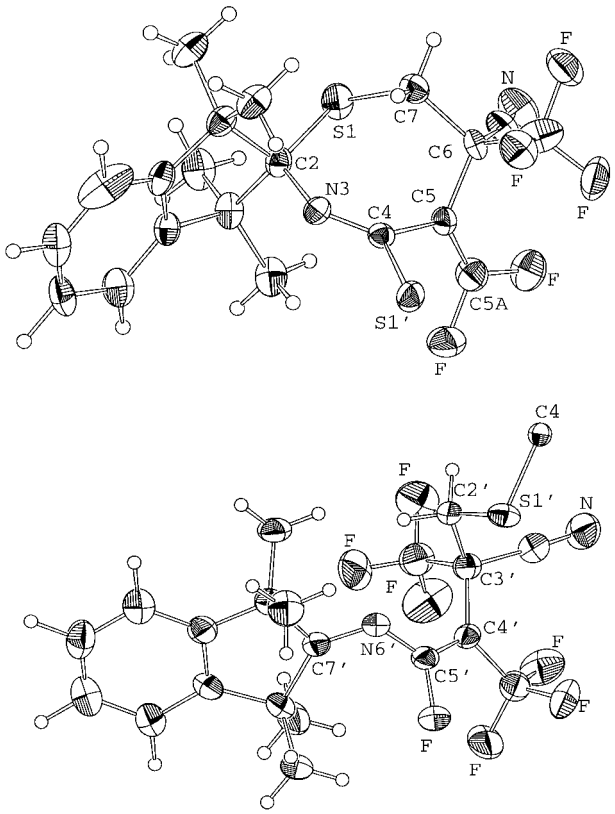


Figure 1. Structure of dimer (6*SR*,3′*RS*)-**13** (**13A**, ZORTEP plot; thermal ellipsoids at 30% probability level); C4–S1′ is the common link between the two halves. Selected bond lengths [Å]: S1–C2 1.832(4), C2–N3 1.445(5), N3=C4 1.250(5), C4–C5 1.494(5), C5=C5a 1.2995(5), C5–C6 1.536(5), C6–C7 1.550(6), C5a–F 1.318(5), 1.323(4), C4–S1′ 1.795(4), S1′–C2′ 1.794(3), C2′–C3′ 1.563(5), C3′–C4′ 1.527(6), C4′=C5′ 1.336(6), C5′–F 1.340(5), C5′–N6′ 1.364(6), N6′=C7′ 1.274(4), C6–CF_3 1.529(5), C3′–CF_3 1.536(5), C4′–CF_3 1.505(6); selected bond angles [°]: S1-C2-N3 115.5(2), C2-N3-C4 131.5(3), N3-C4-C5 131.0(3), C4-C5-C6 119.3(3), C5-C6-C7 109.5(3), C6-C7-S1 109.1(2), C7-S1-C2 100.9(2), F-C5a-F 108.2(3), C4-S1′-C2′ 101.4(2), C3′-C4′-C5′ 123.4(4), C4′-C5′-N6 128.5(4), C5′-N6′-C7′ 126.3(4), F-C5′-N6′ 113.7(3).

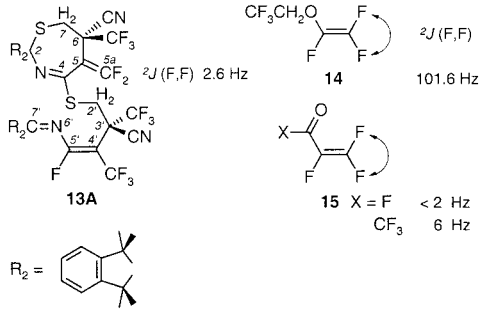
The dihedral angle N3=C4–C5=C5A amounts to 58.6°; the conjugation is weakened by the buckled structure of the seven-membered ring. The Southern part contains an azabutadiene system which is twisted at the C5′–C6′ bond by 45.7°. The van der Waals pressure of the spirosystem is responsible for long C–C bonds in the Northern indane ring (1.594, 1.591 Å), a phenomenon known from related heavily substituted indan-spiro-thiolanes.[11]

The bond C5=CF_2 in **13A** (1.299 Å) is even shorter than in 1,1-difluoroethene (1.316 Å, gas phase, electron diffraction and microwave data[12]). Not less remarkable is the angle F-C5a-F 108.2° at the sp^2-hybridized C-atom which finds a parallel in 1,1-difluoroethene: F-C-F 109.7 and H-C-H 119.3°. This F-C-F angle contraction at olefinic C-atoms found much attention in the past (review:[13]). Furthermore, the C–CF_3 bond length at the saturated C-atoms C6 and C3′ (1.529, 1.536 Å) is found shorter by 0.03 Å for CF_3 at the olefinic C4′ (1.505 Å).

Two stereogenic centers (C-6, C-3′) convey diastereotopicity to the methyl groups in both indane systems. The ^1H and ^{13}C parameters of eight methyl groups reveal two pairs of

isochronous signals which suggest a time-averaged symmetry element in one of the indane residues. Fast *rotation* at the N6′=C7′ bond could confer pairwise identity to the methyl groups in the Southern indane. However, an elegant DNMR study of 2,2,5,5-tetramethylcyclopentylidene N-arylimines, a related model system, by Knorr et al.[14] established *N-inversion* (lateral shift). In the case of **13**, N-inversion would lead to a *cis*-2-azabutadiene which should provide a second set of non-equivalent methyl groups. The isochronism of some methyl signals could well be coincidental.

The H-decoupled ^{19}F NMR spectrum of **13A** shows integrals in the ratio of 1:1:1:3:3:3. The CF_3 groups at the saturated C-3′ and C-6 resonate at lower frequencies. On the high-frequency side, the signals of the olefinic 5′-F and 4′-CF_3 are adjacent, and their coupling with ^4J(F,F) = 23.8 Hz is normal. Only one of the two 5a-F atoms couples with 6-CF_3; Figure 1 exhibits the different distances. The ensemble of multiplicities and F,F-coupling constants allows an unequivocal assignment, but at first the small ^2J(F,F) = 2.6 Hz for =CF_2 in position 5a (F,F distance 2.14 Å) appeared as a stumbling block, since it is not in line with the concept of through-space coupling (review: ref. [15]). In fact, values of ^2J(F,F) vary widely and are very sensitive to substituents, due to large anisotropy effects with positive and negative contributions.[16] Among trifluorovinyl compounds, **14** has a high ^2J(F,F), whereas the β-carbonyl derivatives **15** stand at the low end[17] (Scheme 3). The difluorovinylidene group of **13A** has a β-C=N double bond, thus showing a remote relation to **15**.

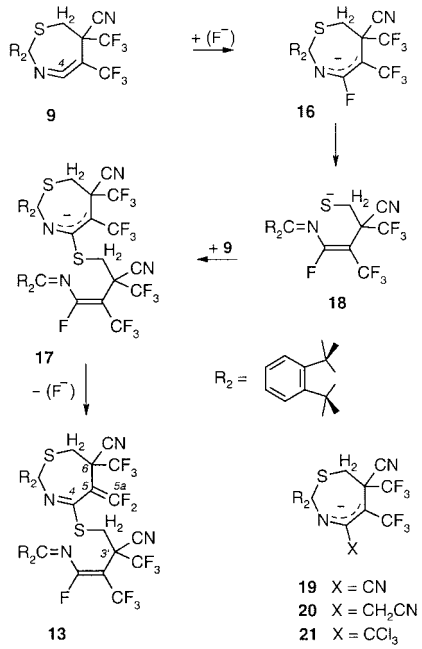


Scheme 3. Dimer **13A** ≡ (6*SR*,3′*RS*)-**13** and comparison with ^2J(F,F) values of trifluorovinyl compounds.

The NMR spectra of **13A** and **13B** are rather similar and in harmony with diastereoisomerism. Among the ^{19}F chemical shifts, the two vinylic 5a-F present the greatest differences.

The configuration shown in Figure 1 is identified as (6*S*,3a′*R*)-**13**, and the centrosymmetric space group of the unit cell indicates two molecules of each enantiomer. When (*R*)-**9** and (*S*)-**9** enter the dimerization process, in principle, the two *rac*-dimers, (6*SR*,3′*RS*) = **13A** and (6*SR*,3′*SR*) = **13B**, may be formed with different rates. However, the ratio **13A**/**13B** = 1:1 (within analytical limits) suggests random combination of (*R*)-**9** and (*S*)-**9**. Racemic dimer (6*SR*,3′*RS*)-**13** has the lower solubility and was isolated pure.

The various reactions of **9** illustrated in Scheme 2 disclose the zwitterion **8** as *deus ex machina*, but **8** does probably not occur on the mechanistic pathway leading to **13**. A rationalization with an ionic chain reaction and the fluoride anion as transfer reagent is presented in Scheme 4. Fluoride—the deviating initiation step will be discussed below—attacks C-4, that is, the electrophilic center of ketene imine **9**, and affords the cyclic aza-allyl anion **16**. Ring opening generates **18** which holds an azabutadiene system and a thiolate function. The latter reacts with C-4 of a second molecule of **9**, thus providing **17**. The loss of the anionic charge is achieved by elimination of fluoride from the 5-CF_3 of **17** and formation of the *exo*-difluoromethylene group of **13**. A formal fluoride is transferred to another molecule of **9**, and a new cycle is started. The different behavior of the cyclic anions **16** and **17** is an open problem.



Scheme 4. Suggested pathway for the base-catalyzed dimerization of the cyclic ketene imine **9**.

In the initiation with KCN, the cyanide adds to the C-4 of **9** and sets the cascade in motion. The cyclic anion **19** furnishes a "dimer" molecule **13** in which 5′-F is replaced by 5′-CN. With the fluoride transfer to **9**, the chain reaction starts, as described in Scheme 4. In the KCN-catalyzed process in acetonitrile, the involvement of the lyate ion NC-CH_2^- is improbable (pK_a in DMSO: HCN 12.9, MeCN 31.3).[18]

1,8-Bis(dimethylamino)naphthalene is a stronger base than triethylamine, but non-nucleophilic.[19] With a pK_a of 18.18 in acetonitrile[20] and an autoprotolysis constant of 3×10^{-29} for this solvent,[21] a 0.06 M solution of "proton sponge" is approximately 2×10^{-6} M in NC-CH_2^-, sufficient to trigger the ionic chain via **20**. Proton sponge in $CHCl_3$ as solvent also initiated dimerization. A deprotonation of $CHCl_3$ is likely; according to a recent compilation,[22] the acidity of $CHCl_3$ exceeds that of MeCN by four pK_a(H_2O) units.

Experimental Section

General:[23] ^{19}F NMR spectra (90.6 MHz) were taken with a Bruker spectrometer; $CFCl_3$ served as internal frequency standard. (1,1-Dichloro-2,2,2-trifluoroethyl)benzene (δ −78.2 ppm; abbreviated "dichlo") was used as weight standard for quantitative analysis (± 5% relative). Vapor phase osmometer: Mechrolab 301A.

2,3,6′,7′-Tetrahydro-4′,5′-didehydro-1,1,3,3-tetramethyl-5′,6′-bis(trifluoromethyl)-spiro[1*H*-indene-2,2′(2*H*)-[1,3]thiazepine]-6′-carbonitrile (9), see ref. [9].

Dimerization of ketene imine 9: a) Crystalline **9** (440 mg, 1.02 mmol), dissolved in dry MeCN (1 mL) at room temperature, was stirred with KCN (~10 mg). Although the catalyst remained undissolved, the yellow solution lighted up in 15 min. After diluting the supersaturated solution 1:1 with $CDCl_3$ and removing KCN by filtration, the ^{19}F NMR spectrum showed the disappearance of **9** and the formation of **13A** and **13B** in the ratio 48:52 (integrals of q 3′-CF_3 + d 6-CF_3, see below). The solvent was evaporated, and the residue recrystallized from hot MeCN: **13** (384 mg, 89%) was obtained in two fractions. The first consisted of **13A** as colorless needles, m.p. 205–207 °C, and the second fraction, m.p. 174–175 °C, contained **13A/13B** ~15:85 (^{19}F NMR signals of d 5a-F at −60.6 and −63.0 ppm).

b) Ketene imine **9** (204 mg, 0.47 mmol) and 1,8-bis(dimethylamino)naphthalene ("proton sponge", 10 mg, 48 μmol) were treated in dry MeCN (0.7 mL). After 2 min at room temperature, the crystallization of **13** set in, and after 1 h, addition of the same volume of $CDCl_3$ led to a clear solution. ^{19}F NMR analysis with "dichlo" provided 77% of **13A** + **13B**. According to the integrals of 5a-F, the ratio was **13A/13B** = 53:47; more reliable is 50.4:49.6 based on q 3′-CF_3 + d 6-CF_3.

c) Ketene imine **9** (0.53 mmol) in $CDCl_3$ (0.5 mL) was treated with proton sponge (69 μmol). After 20 min at room temperature, the ^{19}F NMR analysis with "dichlo" showed **9**/**13** 27:73. No **9** was left after 100 min, and the yield of **13** was 89%. The CF_3 integrals indicated **13A**/**13B** 51.5:48.5.

Properties of dimer 13A: ^{1}H NMR (360 MHz): δ = 1.27, 1.29, 1.39 (3 s, 3 Me), 1.41, 1.43 (2 s, 2×2 Me), 1.53 (s, Me), 3.23, 3.37 (sharp AB, ^2J(H,H) = 14.8 Hz, B branch further split with J(H,F) = 1.7 Hz, 7-H_2), 3.61, 3.80 (less sharp AB, ^2J(H,H) = 13.5 Hz, 2′-H_2), 7.07–7.11, 7.18–7.21, 7.30–7.33 ppm (3 m 2:4:2, 8 arom. CH); ^{13}C NMR (20.2 MHz, not fully resolved): δ = 24.2, 26.0, 27.1 (2×), 28.2, 28.4 (2×), 30.8 (6 q, 8 Me), 30.9 (t, CH_2), 50.9 (s, 2 C_q), 53.2, 55.9, 77.2, 90.4 (4 s, 4 C_q), 113.0, 113.7 (2 s, 2 CN), 121.8, 122.4 (3×), 127.3, 127.4, 128.3 (2×) (5 d, 8 arom. CH), 123 (2 or 3 q, ^1J(C,F) ~280, 2 or 3 CF_3), 146.5 (t or dd), 145.1 (2×), 147.1, 148.2, 172.8, 206.9 ppm (5 s, 6 C_q); ^{19}F NMR (94.2 MHz, ^{1}H-decoupled): δ = −53.5 (q, ^4J = 23.8 Hz, 5′-F), −54.5 (dq, ^4J = 23.7, ^5J ~5 Hz, 4′-CF_3), −60.5 (d, ^2J = 2.5 Hz, 5a-F), −69.1 (dq, ^2J = 2.6 Hz, ^5J = 5.3 Hz, 5a-F), −72.65 (q, ^5J = 4.9 Hz, 3′-CF_3), −72.76 ppm (d, ^5J = 5.3 Hz, 6-CF_3); IR (KBr): ν = 756 m (arom. out-of-plane deform.), 1136 s, 1198 vs, 1244 s, 1313 s, 1325 s (C–F stretch.), 1452 m, 1484 m, 1590 w (arom. ring vibr.), 1626 s, 1666 vs, 1710 vs (C=N, enamine-C=C), 2260 cm^{-1} vw (C≡N); MS (140–150 °C): m/z (%): 864 (35) $[M]^+$, 849 (1) $[M-Me]^+$, 795 (12) $[M-F]^+$, 451 (9) $[M/2+F]^+$, 432 (7) $[M/2]^+$, 417 (8) $[M/2-Me]^+$, 413 (80) $[M/2-F]^+$, 363 (10) $[M/2-CF_3]^+$, 204 (9) $[C_{13}H_{16}S]^+$, 172 (91) $[C_{13}H_{16}]^+$, 171 (100) $[C_{13}H_{15}]^+$, 156 (60) $[C_{12}H_{12}]^+$, 149 (27), 141 (22), 109 (24), 97 (28), 95 (33), 69 (32) $[CF_3]^+$, 55 (48); elemental analysis calcd (%) for $C_{40}H_{36}F_{12}N_4S_2$ (864.85): C 55.56, H 4.20, N 6.48; found C 55.62, H 4.23, N 6.59; molecular mass (vapor phase osmometry, $CHCl_3$): 819.

Properties of dimer 13B: ^{1}H NMR (360 MHz): δ = 1.18, 1.41 (2 q, 2 Me), 1.42, 1.44 (2 q, 2×2 Me), 1.46, 1.53 (2 q, 2 Me), 3.27, 3.35 (AB, ^2J(H,H) = 14.9 Hz, left branch split by J(F,H) = 1.5 Hz, 7-H_2), 3.81 (br s, 2′-H_2), 7.13–7.35 ppm (3 m, 8 arom. CH); ^{19}F NMR (94.2 MHz, ^{1}H-decoupled): δ = −53.3 (q, ^4J = 23.1 Hz, 5′-F), −54.4 (m, unresolved, 4′-CF_3), −63.0 (m, unresolved, 5a-F), −69.6 (dq, ^5J = 4.9, ^2J = 1.5 Hz, 5a-F), −72.2 (q, ^5J = 5.3 Hz, 3′-CF_3), −72.4 ppm (d, ^5J = 4.9 Hz, 6-CF_3); IR and MS: similar to **13A**; elemental analysis calcd (%) for $C_{40}H_{36}F_{12}N_4S_2$ (864.85): C 55.56, H 4.20, N 6.48; found C 55.64, H 4.17, N 6.44.

X-ray diffraction analysis of 13A (Figure 1): monoclinic, space group $P2_1/n$(14). Unit cell dimensions: a = 906.5(3), b = 2939.0(7), c = 1561.1(3) Å, β = 104.67(2)°, V = 4023.6 Å3, Z = 4, ρ_{calcd} = 1.428 g cm^{-3}, $F(000)$ = 1776, T = 294(2) K, μ = 2.136 cm^{-1}. Data collection; ENRAF-Nonius diffractometer CAD4 operating with $Mo_{K\alpha}$ radiation, λ = 0.71069 Å, crystal mounted in a glass capillary, ω-2θ scan, scan width 0.80° + 0.349 tanθ, maximum measuring time 180 s, range $4 < 2\theta < 48°$ for all $\pm h$, $+k$, $+l$ reflections; 7490 reflections collected, 5004 independent, and $3007 > 2\sigma(I)$; three standard reflections checked every 2 h; refined parameters 529. Structure solution by SHELXS-86 and refinement by SHELXL-93.[24] Final $R1$ = 0.0451 and $wR2$ = 0.1178 for 3007 reflections with $I > 2\sigma(I)$. Weight: SHELXL-93. Maximum and minimum of the final difference Fourier synthesis +0.20 and −0.17 e $Å^{-3}$. Non-H atoms were refined anisotropically with inclusion of H-atoms in calculated positions and fixed isotropic U; ZORTEP plot.[25]

CCDC-233 192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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