Silicon Compounds with Strong Intramolecular Steric Interactions, 68[◇]

Silylene Reactions with Nitrogen Multiple Bonds: Additions and Rearrangements☆

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Reactions of the sterically encumbered silylenes R_2Si: (R = 2,4,6-$Me_3C_6H_2$, 2,4,6-$iPr_3C_6H_2$) with azobenzene are thought to proceed via the [2+1] cycloaddition products, followed by insertion of the N–N single bond into the *ortho*-C–H bond of one of the phenyl rings or into the C–HMe_2 bond of one of the *ortho*-isopropyl groups to furnish the 1,3-diaza-2-silaindan (**4**) or 1-aza-2-silaindan (**5**) derivatives, respectively. The reactions of these silylenes with 1-adamantyl azide seem to proceed through the silanimines and 4-azahomoadamantene intermediates which, by [2+2] cycloadditions, afford the 1,3-diaza-2-silacyclobutane derivatives **11** and **12**. The structures of **4**, **5**, **11**, and **12** were determined by X-ray crystallography.

Introduction

The addition of silylenes, R_2Si:, to homo- and heteronuclear multiple bonds is now an established method for the preparation of three-membered ring systems containing silicon atoms. The reactions are particularly facilitated by the presence of bulky alkyl or aryl groups which hinder subsequent rearrangements of the primarily formed three-membered rings.[2][3] However, the course of silylene addition to nitrogen−nitrogen double bonds is still somewhat ambiguous. Even though the first − and as yet only − diazasilirane of the type **3** was prepared in 1982 by a different route,[4] a structural characterization of this three-membered ring system has not yet been achieved. Recently, Ando et al.[5] reported on the photolysis of hexamesitylcyclotrisilane, which is known to decompose into dimesitylsilylene and tetramesityldisilene on exposure to light,[6] in the presence of azobenzene. Although the [2+2] cycloaddition product of the disilene to the N=N double bond was completely characterized, the putative [2+1] cycloaddition product of the silylene was only obtained in the form of a hydrolysis product of the diazasilirane ring system.

We now describe the reactions of two diarylsilylenes bearing sterically demanding substituents with azobenzene and with 1-adamantyl azide (**6**) and the unusual addition and rearrangement products isolated thereby.

Results and Discussion

Irradiation of a solution of the trisilane **1**, which results in the silylene R_2Si: (R = 2,4,6-$Me_3C_6H_2$) together with hexamethyldisilane, in the presence of azobenzene furnished, after separation of a brown oil, colorless crystals for which the analytical and mass-spectral data were in agreement with reported values[2][5] suggestive of a 1:1 adduct of type **3**. However, the NMR- and IR-spectral data were not concordant with this proposal because they demonstrated, for example, the presence of an N−H bond in the molecule. The structure of this addition product was elucidated by X-ray crystallography which revealed that the bicyclic system **4** with a 1,3-diaza-2-silaindan skeleton (Figure 1) had been formed instead of the expected three-membered ring compound **3**.

The reaction of dimesitylsilylene with azobenzene presumably proceeds through an addition of the electron-sextet species to the N=N double bond to furnish **3** as an intermediate. The well-known weakness of the N−N single bond[7] which in this case will experience a further lowering of the bond dissociation energy by its incorporation into a strained three-membered ring probably provides the driving force for the cleavage of this bond with the simultaneous formation of one N−H and one N−C bond. The result is the more or less strain-free five-membered ring part of the bicyclic compound **4**. Surprisingly, this simple bicyclic compound apparently represents the first example of a novel ring system. A search of the Cambridge Crystallographic

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[◇] Part 67: See ref.[1].

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Scheme 1

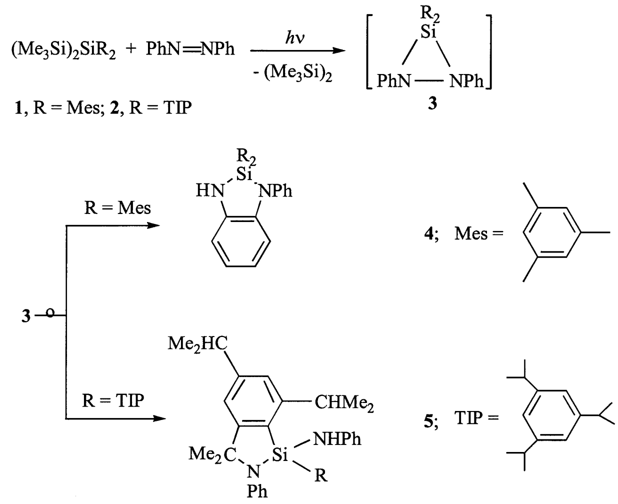
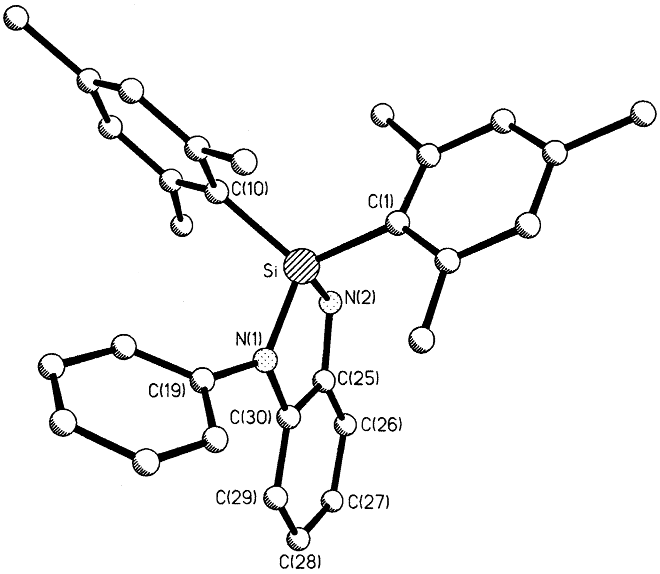


Figure 1. Molecular structure of **4** in the crystal (hydrogen atoms omitted)[a]



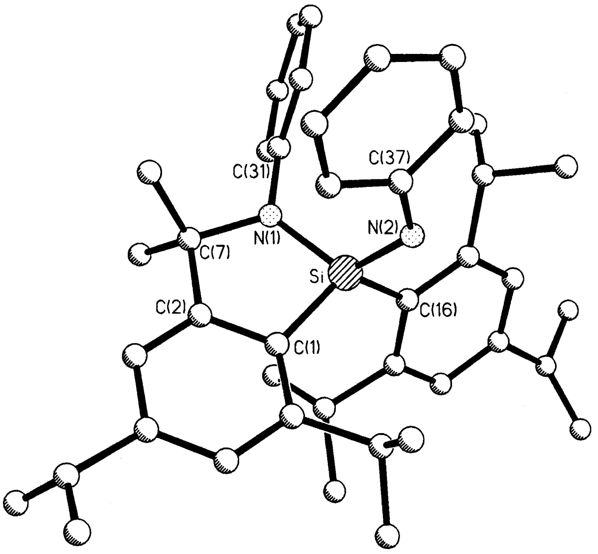
[a] Selected bond lengths [pm] and angles [°]: Si−C(1) 191.7(5), Si−C(10) 192.5(5), Si−N(1) 174.9(8), Si−N(2) 173.1(7); N(1)−Si−N(2) 90.8(4).

Data File revealed only one novel silylene with a similar atomic arrangement.[8]

In order to determine whether this reaction behavior is applicable to other silylenes, we allowed the trisilane **2**, photolysis of which furnishes hexamethyldisilane and the sterically highly overcrowded bis(2,4,6-triisopropylphenyl)silylene, to react with azobenzene under otherwise identical conditions. We isolated a light yellow crystalline product whose elemental analysis and mass-spectral data were again indicative of a 1:1 adduct of the starting materials. However, similarly to compound **4**, the spectroscopic data did not support the formation of an azadisilirane **3** as reaction product. The first assumption of a product analogous to **4** was not confirmed by the X-ray-crystallographic analysis (Figure 2). Although product **5** also contains a five-membered ring as a part of a bicyclic system, the product is not formed by insertion of the nitrogen atom into the *ortho*-C−H bond of the phenyl ring but rather by insertion into a methine C−H bond of one of the *ortho*-isopropyl groups. Assuming the siladiazirane **3** as an intermediate, the subsequent preferred reaction course apparently depends on the bulk of the substituents at the silicon atom and leads to the product with the least ring strain.

With regard to the relatively low yields of **4** (33%) and **5** (17%) it is obvious that several competitive reactions occur which, however, could not be elucidated.

Figure. 2. Molecular structure of **5** in the crystal (hydrogen atoms omitted)[a]

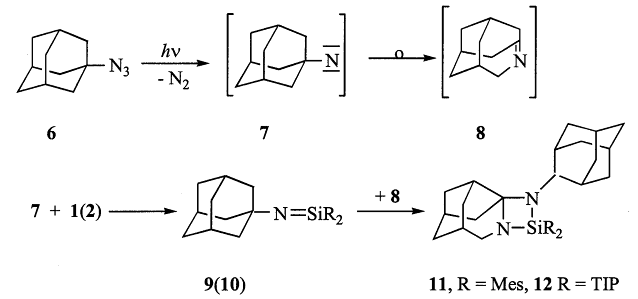


[a] Selected bond lengths [pm] and angles [°]: Si−C(1) 186.1(4), Si−C(16) 194.6(4), Si−N(1) 172.0(6), Si−N(2) 173.4(6); N(1)−Si−N(2) 116.8(3), C(1)−Si−C(16) 124.1(2).

A different form of nitrogen−nitrogen multiple bond is present in the covalent azides and can be described by the two mesomeric forms $R-N=N^+=N^- \leftrightarrow R-N^-=N^+\equiv N$. Which of the two forms dominates depends strongly on the nature of the substituent R.[9] A few years ago we investigated the reactions of the sterically overcrowded tri-*tert*-butylsilyl azide with silylenes bearing voluminous substituents. These reaction were assumed to proceed through cleavage of molecular nitrogen to the nitrene $t\text{Bu}_3\text{Si}-\text{N}$ and reaction of this species with the silylenes to furnish the silanimines $t\text{Bu}_3\text{Si}-\text{N}=\text{SiR}_2$. Most of these products, however, proved to be unstable and underwent various subsequent reactions. Thus, for example, the product obtained from dimesitylsilylene undergoes [1,5]-hydrogen shift followed by a conrotatory electrocyclic ring closure to afford a silacyclobutene derivative.[10] The reactions of 1-adamantyl azide (**6**) with the trisilanes **1** and **2** described in the present paper follow a completely different and previously unobserved course.

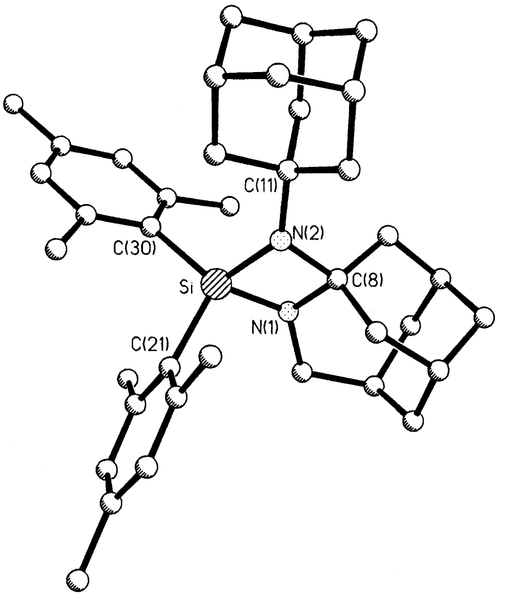
Cophotolysis of **6** and the trisilane **1** affords, through cleavage of nitrogen and hexamethyldisilane, colorless crystals of a compound shown by elemental analytical and spectroscopic data to be a 2:1 adduct of the nitrene **7** and dimes-

Scheme 2



itylsilylene. The constitution of the isolated, crystalline product was elucidated by X-ray crystallography (Figure 3) and unexpectedly found to be that of the 1,3-diaza-2-silacyclobutane derivative **11** in which one of the nitrogen atoms is incorporated into a 4-homoazaadamantane unit.

Figure. 3. Molecular structure of **11** in the crystal (hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°] for **11** and **12**: For **11**: Si−N(1) 173.6(5), Si−N(2) 173.3(4), N(1)−C(8) 147.7(7), N(2)−C(8) 150.0(7); N(1)−Si−N(2) 77.6(2), Si−N(1)−C(8) 94.4(3), N(1)−C(8)−N(2) 93.8(4), Si−N(2)−C(8) 93.7(3). For **12**: Si−N(1) 172.7(4), Si−N(2) 172.5(4), N(1)−C(8) 148.7(5), N(2)−C(8) 151.1(5); N(1)−Si−N(2) 78.8(2), Si−N(1)−C(8) 93.5(2), N(1)−C(8)−N(2) 93.9(3), Si−N(2)−C(8) 92.7(2).

In order to explain the formation of **11** it must be assumed that two parallel reactions with similar reaction rates occur. Firstly, the azide **6** is transformed via the nitrene **7** to the 4-azahomoadamantan-3-ene (**8**). The occurence of the latter intermediate upon photolysis of **6** has been confirmed by numerous trapping reactions.[11] Concomitantly, the silylene generated from the trisilane reacts with another molecule of nitrene **7** to furnish the silanimine **9**. A [2+2] cycloaddition of the two intermediates **8** and **9** would then provide a plausible rationale for construction of the novel polycyclic ring system **11**.

The differing reaction behaviors of **1** and **2** in cophotolysis with azobenzene prompted us to allow the silylene bearing sterically more demanding substituents generated from **2** to react with the azide **6**. Irradiation of a mixture of the two components furnished colorless crystals consisting, similarly to the case of **11**, of a 2:1 adduct of the nitrene **7** and the silylene. Once again, the complicated NMR spectra did not furnish diagnostic information about the structure of the isolated compound. However, X-ray crystallography did indeed reveal that the structure of the product **12** was analogous to that of **11** so that a separate view of the structure is not necessary.[12] Compound **12** is also presumed to be the result of an analogous reaction sequence while the somewhat higher yield (**12**: 38%; **11**: 25%) is attributed to the higher stability of the silanimine **10**.

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Experimental Section

All manipulations were performed under dry nitrogen or argon by using Schlenk techniques. Solvents were purified, dried, and distilled under argon. − ^{1}H, ^{13}C, and ^{29}Si NMR: Bruker AM 300 or Bruker AMX 300. − MS: Varian MAT 212. − IR: Bio-Rad FTS-7. − Elemental analyses: Analytische Laboratorien, D-51779 Lindlar, Germany. − Photolyses were carried out by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

3-Phenyl-2,2-bis(2,4,6-trimethylphenyl)-1,3-diaza-2-silaindan (**4**): At room temp., a solution of **1** (0.41 g, 1.0 mmol) and azobenzene (0.19 g, 1.0 mmol) in 80 ml of *n*-pentane was irradiated for 6 h. After this time, the volatile compounds were distilled off and the residue redissolved in a minimum amount of *n*-pentane. Cooling to −50°C provided a brown oil which was separated by decantation. Cooling of the remaining solution at −30°C furnished 0.150 g (33% yield) of colorless, air-sensitive crystals of **4**, m.p. 171°C. − ^{1}H NMR (C_6D_6): δ = 2.03 (s, 6 H), 2.25 (s, 12 H), 3.6 (s, 1 H, NH), 6.45−7.39 (m, 9 H), 6.63 (s, 4 H). − ^{13}C NMR (C_6D_6): δ = 21.01, 24.11, 111.21, 112.08, 118.17, 119.77, 124.67, 127.34, 129.23, 129.76, 134.07, 138.96, 139.61, 140.19, 143.12, 143.27. − MS (CI, isobutane); *m/z* (%): 449 (100) [MH$^+$]. − IR (nujol): $\tilde{\nu}$ [cm^{-1}] = 3418 (w, NH). − $C_{30}H_{32}N_2Si$ (448.67): calcd. C 80.30, H 7.18; found C 80.16, H 7.13.

[5,7-Diisopropyl-3,3-dimethyl-2-phenyl-1-(2,4,6-triisopropylphenyl)-2-aza-1-sila-1-indanyl]phenylamine (**5**): A solution of **2** (0.58 g, 1.0 mmol) and azobenzene (0.19 g, 1.0 mmol) in 80 ml of *n*-pentane was irradiated for 7 h at room temp. All volatile compounds were distilled off and the residue was redissolved in a minimum amount of *n*-hexane. Cooling at −30°C afforded 0.110 g (17% yield) of pale yellow crystals of **5**, m.p. 158°C. − ^{1}H NMR (C_6D_6): δ = 1.00 (d, 6 H, $^{3}J_{H,H}$ = 6.35 Hz), 1.17 (d, 6 H, $^{3}J_{H,H}$ = 7.0 Hz), 1.22 (d, 6 H, $^{3}J_{H,H}$ = 7.0 Hz), 1.24 (d, 6 H, $^{3}J_{H,H}$ = 7.0 Hz), 1.33 (d, 6 H, $^{3}J_{H,H}$ = 6.35 Hz), 1.55 (s, 3 H), 1.60 (s, 3 H), 2.72 (sept, 1 H), 2.84 (sept, 1 H), 3.21 (sept, 1 H), 3.60 (br., 2 H), 4.45 (s, 1 H, NH), 6.63−7.10 (m, 10 H), 7.15 (s, 2 H), 7.22 (s, 1 H), 7.24 (s, 1 H). − ^{13}C NMR (C_6D_6): δ = 23.30, 23.87, 23.96, 26.02, 29.09, 31.60, 34.18, 34.48, 34.83, 35.89, 65.26 (C_q, ring), 117.69, 118.89, 119.89, 122.14, 125.94, 129.03, 129.41, 129.56, 131.88, 133.86, 143.51, 146.91, 150.60, 151.86, 154.04, 156.99. − ^{29}Si NMR (C_6D_6): δ = −26.82. − MS (CI, isobutane); *m/z* (%): 618

Table 1. Crystallographic data of **4**, **5**, **11**, and **12**

	4	**5**	**11**	**12**
formula	$C_{30}H_{32}N_2Si$	$C_{42}H_{56}N_2Si$	$C_{98}H_{52}N_2Si \cdot C_5H_{12}$	$C_{50}H_{76}N_2Si \cdot 1/2\ C_5H_{12}$
mol. mass	448.67	616.98	637.05	769.92
cryst. dimension [mm]	0.38 × 0.34 × 0.27	0.63 × 0.29 × 0.11	0.68 × 0.49 × 0.38	0.61 × 0.49 × 0.30
cryst. system	orthorhombic	monoclinic	triclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/c$	$P1$	$Pccn$
a [pm]	925.1(2)	2093.8(4)	1149.0(1)	1647.6(1)
b [pm]	971.0(2)	912.8(2)	1172.1(1)	3762.3(3)
c [pm]	2837(1)	1990.2(4)	1543.6(2)	1521.5(1)
α [°]	90	90	74.74(1)	90
β [°]	90	98.48(3)	83.50(1)	90
γ [°]	90	90	70.73(1)	90
V [$\times 10^6$ pm^3]	2549(1)	3762(1)	1892.6(3)	9431.4(1)
Z	4	4	2	8
$d_{\text{calcd.}}$ [g cm^{-3}]	1.169	1.089	1.118	1.084
μ [mm^{-1}]	0.112	0.092	0.093	0.085
scan method	ω	ω-2θ	ω-2θ	ω
2θ(max) [°]	48	42	48	46
no. of unique reflections	2306	4593	5940	6538
no. of observed reflections	1604	2648	4664	3971
parameters	250	349	378	471
R [$I > 2\,\sigma(I)$]	0.081	0.095	0.097	0.085
$wR2$	0.185	0.210	0.263	0.175

(60) [MH$^+$]. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3422 (m, NH). − $C_{42}H_{56}N_2Si$ (616.98): calcd. C 81.70, H 9.14, N 4.54; found C 79.86, H 9.16, N 4.25.

Formation of Compound **11**: A solution of **1** (0.41 g, 1.0 mmol) and **6** (0.36 g, 2.0 mmol) in 80 ml of *n*-pentane was irradiated for 7 h at room temp. All volatile compounds were removed by vacuum distillation and the residue was redissolved in a minimum amount of DME. Cooling at 4°C yielded 0.150 g (25% yield) of colorless crystals of **11**, m.p. 211°C. − ^{1}H NMR (C_6D_6): δ = 1.33−1.81 (accumulation of signals, 15 H), 1.85 (s, 6 H), 1.95−3.13 (accumulation of signals, 27 H), 6.65 (s, 2 H), 6.83 (s, 1 H), 6.88 (s, 1 H). − ^{13}C NMR (C_6D_6): δ = 21.09, 29.57, 30.07, 30.46, 32.92, 34.29, 34.40, 35.50, 36.94, 40.60, 44.93, 47.14, 49.46, 51.25, 53.24, 88.45, 128.30, 128.92, 129.88, 130.14, 136.55, 136.75, 137.55, 139.01, 140.88, 141.32, 143.21, 144.35. − ^{29}Si NMR: δ = −10.52. − MS (CI, isobutane); *m/z* (%): 565 (100) [MH$^+$]. − $C_{38}H_{52}N_2Si$ (564.86): calcd. C 80.80, H 9.28, N 4.96; found C 78.20, H 9.81, N 4.56.

Formation of Compound **12**: At room temp., a solution of **2** (0.52 g, 1.0 mmol) and **6** (0.36 g, 2.0 mmol) in 80 ml of *n*-pentane was irradiated for 8 h, after which the reaction was shown to be complete by the dissappearance of **2** (TLC monitoring). All volatile compounds were distilled off and the residue redissolved in a minimum amount of *n*-pentane. Cooling at 4°C afforded 0.280 g (38% yield) of colorless crystals of **12**, m.p. 242°C. − ^{1}H NMR (C_6D_6): δ = 0.30 (d, br., 6 H), 1.21−1.31 (accumulation of signals, 21 H), 1.31−1.72 (accumulation of signals, 24 H), 1.90−2.90 (accumulation of signals, 15 H), 2.75 (sept, 2 H), 3.09 (sept, 1 H), 3.23 (sept, 1 H), 5.13 (sept, 1 H), 5.68 (sept, 1 H), 6.95 (s, 1 H), 6.96 (s, 1 H), 7.21 (s, 2 H). − ^{13}C NMR (C_6D_6): δ = 23.02, 23.07, 23.10, 24.11, 24.63, 24.92, 25.14, 25.15, 25.52, 26.18, 26.69, 29.18, 29.57, 30.26, 30.50, 30.65, 33.05, 34.47, 34.50, 34.59, 35.10, 35.48, 36.59, 36.83, 40.84, 45.87, 47.38, 50.27, 52.97, 53.29, 87.76, 121.63, 122.47, 122.73, 122.85, 136.34, 136.71, 149.51, 150.50, 152.86, 153.19, 154.10, 155.43. − ^{29}Si NMR (C_6D_6): δ = −10.87. − MS (CI, isobutane); *m/z* (%): 733 (100) [MH$^+$]. − $C_{50}H_{76}N_2Si$ (733.24): calcd. for **12** · 1/2 pentane C 79.96, H 10.11, N 3.72; found C 79.84, H 10.81, N 3.57.

X-ray Structural Analyses of Compounds **4**, **5**, **11**, *and* **12**: Crystal and numerical data of the structure determinations are given in Table 1.[12] In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed at room temp. with a Siemens Stoe AED 2 diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved by direct-phase determination using the Siemens SHELXTL PLUS and SHELX 93[13] program systems and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically.

☆ Dedicated to Professor *Walter Jansen* on the occasion of his 60th birthday.

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[12] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101486. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, U.K. [fax: int. code + (1223)336-023. e-mail: deposit@ccdc.cam.ac.uk].
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