The First Ring-Enlargement of a 1-Azabicyclo[1.1.0]butane to a 1-Azabicyclo[2.1.1]hexane

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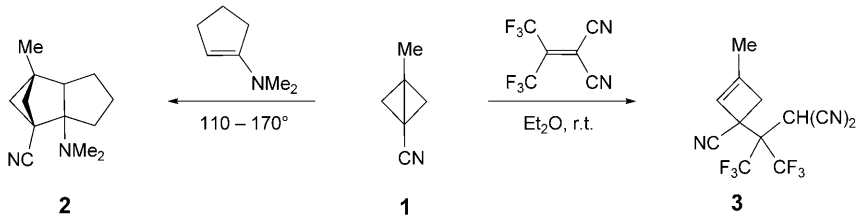
The reactions of 3-phenyl-1-azabicyclo[1.1.0]butane (**4**) with dimethyl dicyanofumarate ((*E*)-**8**) and dimethyl dicyanomaleate ((*Z*)-**8**) lead to the same mixture of *cis*- and *trans*-4-phenyl-1-azabicyclo[2.1.1]-hexane 2,3-dicarboxylates (*cis*-**11** and *trans*-**11**, resp.; *Scheme 3*). This result of a formal cycloaddition to the central C–N bond of **4** is interpreted by a stepwise reaction mechanism *via* a relatively stable zwitterionic intermediate **10**, which could be intercepted by morpholine to give a 1:1:1 adduct **12**, which undergoes a spontaneous elimination of HCN to yield the fumarate **13** (*Scheme 4*).

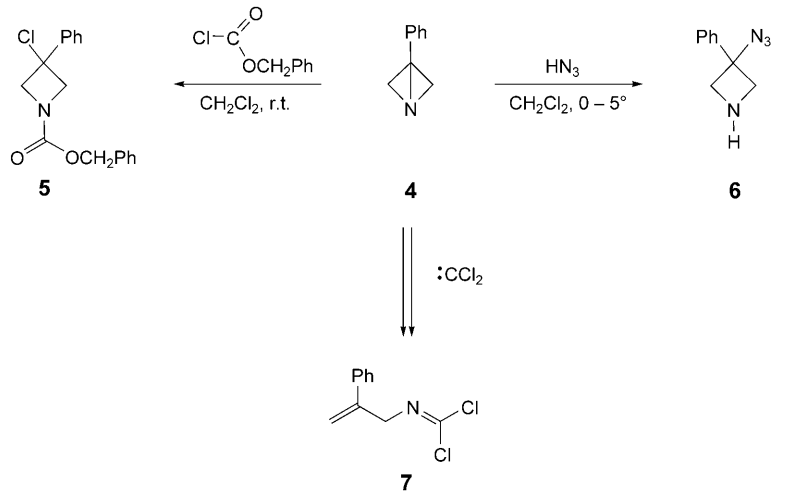
1. Introduction. – Strained bicyclo[1.1.0]butane derivatives are attractive compounds for theoretical and spectroscopic studies [1]. As soon as the first example had been synthesized [2], numerous reports appeared in which differently substituted representatives were explored as useful building blocks for the preparation of cyclobutanes and cyclobutenes [3], as well as larger bicyclic systems. One of the first observations was the ring enlargement to give a bicyclo[2.1.1]hexane *via* a formal cycloaddition with differently substituted ethenes [4]. It turned out that, in the case of 3-methylbicyclo[1.1.0]butane-1-carbonitrile (**1**), the reactions with electron-rich olefins, *e.g.*, *N,N*-dimethylcyclopent-1-en-1-amine, led to the polycyclic adduct **2** in high yield [4] (*Scheme 1*). On the other hand, the electron-deficient 2-[bis(trifluoromethyl)methylidene]propanedinitrile (BTF) afforded the cyclobutene derivative **3** [3]. These reactions are assumed to occur stepwise *via* diradical intermediates.

Scheme 1



In comparison with bicyclo[1.1.0]butanes, the relatively stable 1-aza analogues[1]) are rarely applied as starting materials for the synthesis of N-heterocycles. The main products obtained are azetidines, which are easily formed when 1-azabicyclo[1.1.0]butanes are treated with electrophilic reagents. For example, 3-phenylazabicyclo[1.1.0]butane (**4**) reacts with alkyl chloroformates at room temperature to give 3-chloro-3-phenylazetidine-1-carboxylates of type **5** [6] (*Scheme 2*). A recent report described the smooth addition of hydrazoic acid across the N(1)–C(3) bond to yield **6** [7]. The electrophilic dichlorocarbene reacts with **4** under ring opening to give the *N*-(dichloromethylidene)-2-phenylprop-2-enamine (**7**) [8][2]). Similar results were obtained with (chloro)(phenyl)-carbene and 3-ethyl-1-azabicyclo[1.1.0]butane [10].

Scheme 2



To the best of our knowledge, there are no reports on the reaction of 1-azabicyclo[1.1.0]butanes with alkenes to give cycloadducts or other adducts corresponding to the reactions depicted in *Scheme 1*. The present paper focuses on preliminary results obtained from the reactions of **4** with electron-deficient alkenes.

2. Results and Discussion. – In analogy to other bicyclic tertiary amines, 1-azabicyclo[1.1.0]butanes are expected to be basic[3]) and nucleophilic substances. For this reason, electron-deficient alkenes should readily undergo reactions with 1-azabicyclo[1.1.0]butanes. The first experiment carried out with **4** and BTF in CH_2Cl_2 at 0–5° showed that an exothermic reaction occurs. The product obtained thereby was a thick, colorless oil with all characteristics of a polymeric material. A similar reaction

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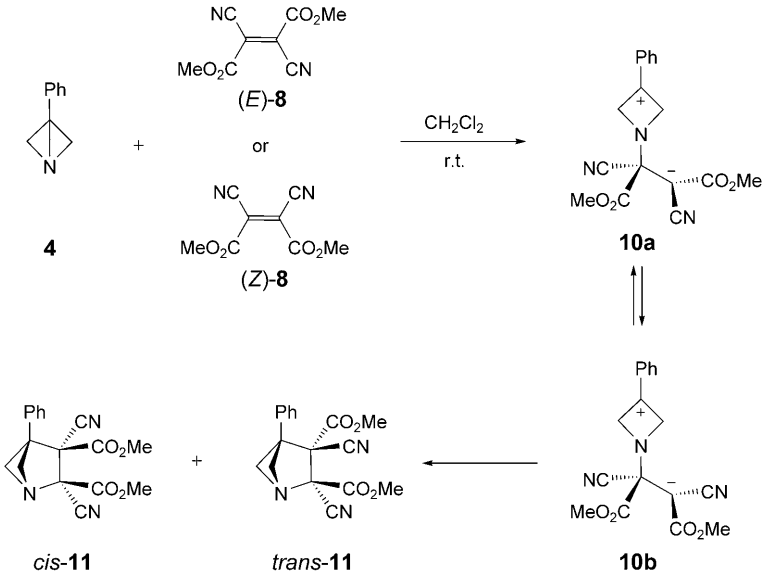
[1]) The first synthesis of 1-azabicyclo[1.1.0]butanes, the parent system, as well as of the 3-methyl and 3-ethyl derivatives, was reported in 1969 [5].

[2]) All attempts to add the nucleophilic dimethoxycarbene to **4** were in vain, and **4** was recovered almost quantitatively [9].

[3]) As far as we know, no physicochemical studies on the basicity of 1-azabicyclo[1.1.0]butanes have been reported.

course was observed in the case of ethenetetracarbonitrile (TCNE). However, when a solution of 1 equiv. of **4** in CH_2Cl_2 was added dropwise to a suspension of 3 equiv. of dimethyl dicyanofumarate (DCFM, (*E*)-**8**; *cf. Scheme 3*) in CH_2Cl_2, the suspension dissolved slowly, and complete conversion of **4** was observed after 4 h.

Scheme 3



The ^{1}H-NMR spectrum of the crude mixture revealed the presence of two new products with two different signals for MeO in each case. The MeO signals of the major product appear at 3.70 and 3.89 ppm, and those of the minor one at 3.88 and 4.10 ppm. Based on the intensity of these signals, a ratio of *ca.* 3:1 was established for the two products. The analogous experiment with **4** and dimethyl dicyanomaleate (DCMM, (*Z*)-**8**), which was very soluble in CH_2Cl_2, led to the same mixture of products. Chromatographic separation on SiO_2 plates gave two fractions as crystalline materials, which, after recrystallization, were identified as two isomeric 1:1 adducts on the basis of their elemental analyses and mass spectra. The major isomer, with m.p. 165–167°, shows a weak IR absorption for C≡N groups at 2241cm^{-1}, and two very strong ester bands at 1777 and 1747 cm^{-1}. The corresponding signals of the minor product (m.p. 138–140°) appear at 2246, 1770, and 1757 cm^{-1}. In the ^{13}C-NMR spectra, both isomers show signals for two non-equivalent ester CO groups (165.5/162.3 and 164.0/162.6 ppm, resp.) and two non-equivalent C≡N groups (115.3/114.6 and 115.4/114.2 ppm, resp.). Additional characteristic signals of the major isomer are those of two CH_2 groups at 66.3 and 62.9 ppm, and three signals for quarternary C-atoms at 77.9, 71.4, and 61.6 ppm. A similar set of signals was found for the minor isomer. Finally, the structure of the major product was established by X-ray crystallography (*Fig.*).

The analysis established the structure of *cis*-**11**, *i.e.*, a 4-phenyl-1-azabicyclo[2.2.1]-hexane with two *cis*-configured C≡N and CO_2Me groups at C(2) and C(3). Consequently, the structure of the minor product is attributed as the *trans*-isomer (*trans*-**11**).

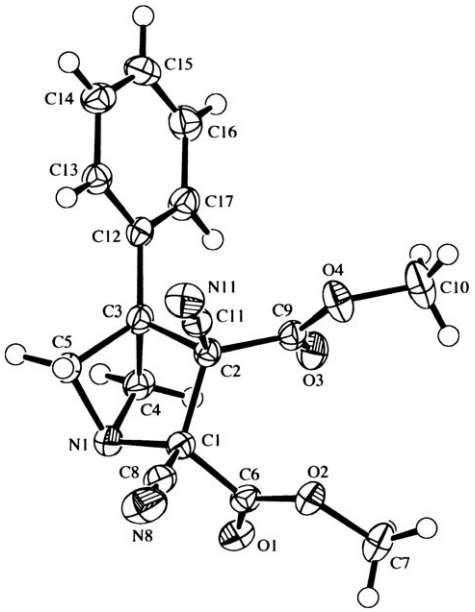
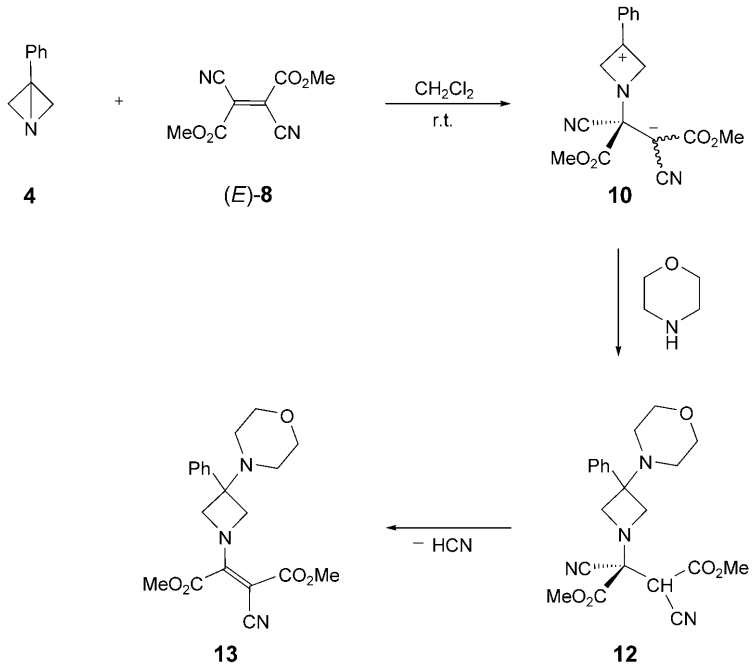


Figure. *ORTEP Plot* [11] *of the molecular structure of* cis-**11** (arbitrary numbering of the atoms, 50% probability ellipsoids)

The formation of the two isomers, *cis*-**11** and *trans*-**11**, in the same ratio, irrespective of the use of (*E*)-**8** or (*Z*)-**8** as the reagent, can be explained by the two-step mechanism presented in *Scheme 3*. The first step of the reaction is the nucleophilic addition of **4** to the activated C=C bond in a *Michael* fashion. In the formed zwitterion **10**, the positive as well as the negative charge are ideally stabilized, which results in the prolongation of the lifetime of this species. Therefore, **10a** derived from (*E*)-**8** and **10b** derived from (*Z*)-**8** are able to equilibrate to give the same mixture. These zwitterions then undergo a cyclization by formation of a new C,C bond to yield the final products **11**. This ring closure is slow in comparison with the rotation about the C,C bond in the zwitterions **10**.

The proposed reaction pathway was additionally supported by the interception of **10** with morpholine. When the reaction of **4** and (*E*)-**8** was performed in the presence of a five-fold excess of morpholine, the formation of a single new product was observed. The compound isolated after chromatographic workup showed in the ^{1}H-NMR spectrum, as well as in the IR spectrum, the presence of two different MeO_2C groups. In addition, a strong C≡N absorption appears in the IR spectrum. The ^{13}C-NMR data confirmed the presence of two non-equivalent ester groups, and, unexpectedly, only one signal for C≡N was detected. Based on these data, and supported by the MS and elemental analyses, the structure was elucidated as **13**, the 1:1:1 adduct after elimination of HCN (*Scheme 4*). The proposed interception product **12** could not be detected, as spontaneous elimination of HCN led immediately to the isolated azetidine derivative **13**.

Scheme 4



In conclusion, the present study showed once more that zwitterions formed by nucleophilic addition to the C=C bond of (*E*)-**8** and (*Z*)-**8** (DCFM and DCMM, resp.) are perfectly stabilized, and their formation determines the pathway of the subsequent reactions. Analogous formations of intermediates have been observed in reactions of (*E*)-**8** and (*Z*)-**8** with thiocarbonyl *S*-methanides [12], as well as with dimethoxycarbene [13]. The presented reaction with 1-azabicyclo[2.1.1]butanes opens a new and convenient access to 1-azabicyclo[2.1.1]hexanes, which are almost unknown. The only report on a synthesis of a representative of this class of 1-azabicycles concerned an alumina-catalyzed rearrangement [14].

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Experimental Part

1. *General.* M.p.: in capillaries (*Melt-Temp. II, Aldrich*); uncorrected. IR Spectra: *NEXUS FT-IR* spectrophotometer; in KBr. ^{1}H- and ^{13}C-NMR spectra: *Tesla BS567A* (80 and 20 MHz, resp.) or *Bruker AC 300* instrument (300 and 75.5 MHz, resp.), in $CDCl_3$; TMS as an internal standard. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instruments ($CI(NH_3)$).

2. *Starting Materials. 3-Phenyl-1-azabicyclo[1.1.0]butane* (**4**) was obtained from 3-phenyl-2*H*-azirine *via* addition of a sulfonium ylide according to [15]. *Dimethyl dicyanofumarate* (DCFM, *dimethyl (*E*)-2,3-dicyanobut-2-enedioate*, (*E*)-**8**) was prepared from commercially available methyl cyanoacetate by heating in excess $SOCl_2$ following the protocol in [16]. *Dimethyl dicyanomaleate* (DCMM, *dimethyl (*Z*)-2,3-dicyanobut-2-enedioate*, (*Z*)-**8**) is conveniently available by photolysis of a DCFM solution in CH_2Cl_2 with a high-pressure Hg lamp and a *Pyrex* filter [17]. *2-[Bis(trifluoromethyl)methylidene]propanedinitrile* (BTF) was prepared following the protocol in [18]. *Ethenetetracarbonitrile* (TCNE) was used as a commercial reagent after purification by sublimation *in vacuo*.

3. *Reactions of* **4** *with Electron-Deficient Ethenes. General Procedure.* A soln. of **4** (131 mg, 1 mmol) in CH_2Cl_2 (1 ml) was dropped slowly into a stirred and cooled (water/ice bath) soln. of the appropriate ethene derivative (1 mmol) in CH_2Cl_2 (2 ml). The reactions with BTF and TCNE occurred exothermally and were complete as soon as the addition was finished. In the experiments with DCMF and DCMM, the cooling bath was removed after 1 h, and stirring was continued for 4 h at r.t. After evaporation of the solvent, oily residues were analyzed by means of ^{1}H-NMR spectroscopy. Polymeric products obtained with BTF and TCNE were neither purified nor identified. The mixtures obtained from the reactions with DCFM and DCMM, respectively, showed identical composition with a *ca*. 3:1 ratio of two new products with characteristic ^{1}H-NMR signals for the MeO groups at 3.89 and 3.70 ppm for the major component, and 4.08 and 3.90 ppm for the minor one. The crude mixtures were preliminarily purified on a short SiO_2 column and subsequently separated on prep. TLC plates coated with SiO_2 by using $CHCl_3$ as the developing solvent. Repeated development was needed to isolate two narrowly separated fractions. The less polar fraction consisted of the minor product identified as *trans*-**11**. Anal. pure samples were obtained by recrystallization.

The reaction with DCMM was performed analogously to the procedure described for DCFM and chromatographic workup led to *trans*-**11** and *cis*-**11** in a *ca*. 3:1 ratio.

Dimethyl cis*-2,3-Dicyano-4-phenyl-1-azabicyclo[2.1.1]hexane-2,3-dicarboxylate* (*cis*-**11**). More polar fraction. Yield: 120 mg (37% after PLC). Colorless crystals. M.p. 165–167° (hexane/CH_2Cl_2). IR (KBr): 2241v*w* (CN), 1777v*s* (C=O), 1747v*s* (C=O), 1450*m*, 1443*m*, 1262v*s* (C–O), 1095*s*, 1085*m*, 1057*m*, 914*m*, 902*m*, 840*m*, 767*m*, 723*m*, 698*s*. ^{1}H-NMR: 7.38–7.35 (*m*, 3 arom. H); 7.12–7.08 (*m*, 2 arom. H); 3.99 (*dd*, *J* = 9.4, 9.3, 1 H); 3.84 (*s*, MeO); 3.77 (*dd*, *J* = 8.0, 8.4, 2 H); 3.70 (*s*, MeO); 3.53 (*dd*, *J* = 8.9, 9.5, 1 H). ^{13}C-NMR: 165.5, 162.3 (2*s*, 2 C=O); 130.7 (*s*, 1 arom. C_q); 129.4, 129.0, 126.1 (3*d*, 5 arom. CH); 115.3, 114.6 (2*s*, 2 CN); 77.9 (*s*, C(2)); 71.4 (*s*, C(3)); 66.3, 62.9 (2*q*, 2 MeO); 61.6 (*s*, C(4)); 54.5, 54.4 (2*t*, 2 CH_2). CI-MS: 343 (6, $[M+NH_4]^+$), 326 (100, $[M+1]^+$). Anal. calc. for $C_{17}H_{15}N_3O_4$ (325.32): C 62.77, H 4.65, N 12.92; found: C 62.61, H 4.68, N 12.83.

Dimethyl trans*-2,3-Dicyano-4-phenyl-1-azabicyclo[2.1.1]-hexane-2,3-dicarboxylate* (*trans*-**11**). Less polar fraction. Yield: 35 mg (10% after PLC). Colorless crystals. M.p. 138–140° (hexane/CH_2Cl_2). IR: 2246v*w* (CN), 1770v*s* (C=O), 1757v*s* (C=O), 1436*m*, 1270v*s* (C–O), 1096*m*, 1059*m*, 750*m*. ^{1}H-NMR: 7.41–7.33 (*m*, 3 arom. H); 7.27–7.19 (*m*, 2 arom. H); 4.08 (*s*, MeO); 3.90 (*s*, MeO); 3.92–3.87 (*m*, 2 H); 3.79–3.69 (*m*, 1 H); 3.63–3.46 (*m*, 1 H). ^{13}C-NMR: 164.0, 162.6 (2*s*, 2 C=O); 130.9 (*s*, 1 arom. C_q); 129.1, 128.8, 127.0 (3*d*, 5 arom. CH); 115.4, 114.2 (2*s*, 2 CN); 78.2 (*s*, C(2)); 68.9 (*s*, C(3)); 66.0, 64.7 (2*q*, 2 MeO); 60.7 (*s*, C(4)); 55.0, 54.7 (2*t*, 2 CH_2). CI-MS: 326 (100, $[M+1]^+$). Anal. calc. for $C_{17}H_{15}N_3O_4$ (325.32): C 62.77, H 4.65, N 12.92; found: C 62.74, H 5.10, N 12.38.

4. *Reaction of* **4** *with (*E*)-***8*** in the Presence of Morpholine.* To a stirred soln. of DCFM ((*E*)-**8**; 194 mg, 1 mmol) and morpholine (435 mg, 5 mmol) in CH_2Cl_2 (1 ml), **4** (131 mg, 1 mmol) dissolved in CH_2Cl_2 (1 ml) was added dropwise at r.t. After 5 h, the mixture was evaporated to dryness, and the evaporation was repeated 2× with small portions of toluene (2×5 ml) in order to remove excess morpholine. The residual thick oil was separated on TLC plates coated with SiO_2 by using CH_2Cl_2/MeOH (88.5:11.5) as the eluting system. A sole fraction with with an R_f value of *ca.* 0.5 was isolated and additionally purified by crystallization.

*Dimethyl (*E*)-{2-[3-(Morpholin-4-yl)-3-phenylazetidin-1-yl]-3-cyano}but-2-enedioate* ((*E*)-**13**). Yield: 340 mg (88% after PLC). Colorless crystals. M.p. 156–158° (MeOH). IR: 2206*m* (CN), 1749*s* (C=O), 1702*s* (C=O), 1570v*s* (C=C), 1452*s*, 1305v*s*, 1264v*s*, 1196*s*, 1150*s*, 1133*s*, 1116*s*, 769*w*, 708*w*. ^{1}H-NMR: 7.44–7.33 (*m*, 3 arom. H); 7.06–7.03 (*m*, 2 arom. H); 4.94, 4.91 (*AB*, *J* = 11.6, CH_2); 4.43, 4.39 (*AB*, *J* = 9.6, CH_2); 3.93 (*s*, MeO); 3.72 (*s*, MeO); 3.73–3.66 (*m*, 2 CH_2O); 2.29–2.24 (*m*, 2 CH_2N). ^{13}C-

NMR: 165.1, 161.8 (2 C=O); 158.2 (C(2)); 134.5 (*s*, 1 arom. C_q); 128.3, 127.1 (2*d*, 5 arom. CH); 116.9 (CN); 70.3 (C_q); 66.8 (2 CH_2O); 63.3 (C_q, C(3)); 62.6, 61.8 (2 CH_2(azetidine)); 53.7, 52.1 (2 MeO); 46.3 (2 CH_2N). CI-MS: 386 (100, $[M+1]^+$), 189 (9). Anal. calc. for $C_{20}H_{23}N_3O_5$ (385.41): C 62.33, H 6.01, N 10.90; found: C 62.21, H 5.94, N 10.84.

5. *X-Ray Crystal-Structure Determination of* cis-**11** (*Table* and *Fig.*)[4]). All measurements were performed on a *Nonius KappaCCD* area-detector diffractometer [19] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [20]. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The structure was solved by direct methods

Table. *Crystallographic Data for* cis-**11**

Crystallized from		hexane/CH_2Cl_2
Empirical formula		$C_{17}H_{15}N_3O_4$
Formula weight		325.32
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.18×0.20×0.30
Temp. [K]		160(1)
Crystal system		Triclinic
Space group		$P\bar{1}$
Z		2
Reflections for cell determination		4543
2θ Range for cell determination [°]		4–60
Unit cell parameters	a [Å]	8.3240(2)
	b [Å]	8.9030(2)
	c [Å]	12.3691(3)
	α [°]	100.752(1)
	β [°]	94.808(1)
	γ [°]	116.114(1)
	V [Å3]	794.20(3)
D_x [g cm^{-3}]		1.360
μ(MoK_α) [mm^{-1}]		0.0990
Scan type		ϕ and ω
$2\theta_{(max)}$ [°]		60
Total reflections measured		21407
Symmetry independent reflections		4602
Reflections with $I>2\sigma(I)$		3979
Reflections used in refinement		4597
Parameters refined		219
Final	$R(F)$ [$I>2\sigma$ (I) reflections]	0.0416
	$wR(F^2)$ (all data)	0.1116
Weighting parameters [a; b][a])		0.0507; 0.2124
Goodness-of-fit		1.038
Final Δ_{max}/σ		0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.33; −0.18

[a]) $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$ where $P=(F_o^2+2F_c^2)/3$.

[4]) CCDC-287053 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request.cif.

using SIR92 [21], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). The refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Five reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [22a], and the scattering factors for H-atoms were taken from [23]. Anomalous dispersion effects were included in F_c [24]; the values for f' and f'' were those of [22b]. The values of the mass attenuation coefficients are those of [22c]. All calculations were performed using the SHELXL97 [25] program.

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