Pyramidalization in Derivatives of Bicyclo[5.1.0]oct-1(7)-enes and 2,2,5,5-Tetramethylbicyclo[4.1.0]hept-1(6)-enes

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Bicyclo[4.1.0]hept-1(6)-ene and bicyclo[5.1.0]oct-1(7)-ene systems have been investigated by X-ray diffraction and ab initio methods. The syntheses of **3b**–**3e**, **4a**, **4b**, **6a**, **7a**, **8b**, **9b**, **12**, **13**, and **16** have been described and the structures of **1**, **3a**, **4b**, **5a**, **7a**, **10**, **11**, and **13**–**16** have been determined by X-ray analysis. To complement these experimental data, several model compounds have been studied theoretically. For the cyclopropenes **14** and **15**, substantial pyramidalization has been observed, and the six-membered ring species is considerably more strongly deformed than the seven-membered ring system [**14**: Φ = 14.5(6)°; **15**: Φ = 30.2(5)°]. Our analysis, with the aid of the model compounds **M-3.OH**, **M-63.H**, **M-63.OH**, **M-73.H**, and **M-73.OH**, clearly shows that the decisive factors for pyramidalization are ring size, conformation, and repulsion between the occupied π bond and the oxygen lone pairs. The last factor contributes to the pyramidalization stemming from ring strain in **14** and is the dominant source of deformation in **15**. In the cyclopropenylidene systems **4b** [Φ = 0.7(4)°], **11** [Φ = 1.1(3)°], **13** [Φ = 4.7(5)°], and **1** [Φ = 7.9(5)°], we have studied the electronic influence on pyramidalization. A high degree of pyramidalization is favored by weak cyclopropenylium character, and cyclopropenylidenes exhibit, in general, smaller deformations than do analogous cyclopropene systems.

Introduction

Since the first pyramidalized alkene was isolated by Weinshenker and Greene in 1968,[1] many similarly deformed alkene compounds have been investigated, both theoretically and experimentally. In pyramidalized alkenes, the doubly bonded carbon atoms do not lie in the plane of the three atoms attached to them; for reviews see Szeimies,[2] Borden,[3] and Luef and Keese.[4] Substituents which are asymmetrical with respect to the local symmetry plane of the π-bond system produce small pyramidalizations of these moieties.[5] A pronounced pyramidalization of the alkene group can be enforced by structural constraints such as short intramolecular links:[6–10] e.g., in bicyclic alkenes of small ring size and with the double bond forming the central bond. Cyclopropenes bridged in the 1,2-position belong to this class of compounds and, so far, only a few compounds of this type have been investigated by X-ray analysis.[11–13] For bicyclic systems, theoretical investigations[14–16] predict on the one hand an increase in pyramidalization with decreasing ring size. On the other hand, it has been found that the degree of deformation in pyramidalized systems depends on the electron density at the pyramidalized atoms;[5,17] a high degree of pyramidalization is favored if the relevant double bond is a component of an electron-rich π system. Our goal is a systematic study of pyramidalization effects in bicyclo[n.1.0]alk-1(n+2)-ene systems, while our structural results should provide a reference for theoretical predictions.

In this section we describe the synthesis of various bicyclic cyclopropenylidenes and cylopropenylidene imines. In addition, bicyclo[5.1.0]oct-1(7)-en-8-one (**1**) and 2,2,5,5-tetramethylbicyclo[4.1.0]hept-1(6)-en-7-one (**2**), together with derivatives of these bicyclic cyclopropenones (Scheme 1), have been studied.

Scheme 1. The structural formulae of cyclopropenones **1** and **2**

Subsequently, the molecular structures of these compounds, as obtained from X-ray analysis, are discussed. The pyramidalization angles Φ of the bridgehead atoms were determined from these data (Φ is the angle between the C=C-bond axis and the R−C−R′ plane as defined in Figure 1).[18] Moreover, several model systems were studied theoretically.

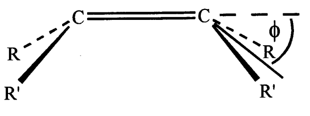

Figure 1. The pyramidalization angle Φ is the angle between the C=C axis and the (C,R,R′) plane; let the positions of C_1, C_2, R, and R′ be defined by the vectors c_1, c_2, r, and r', respectively; then, the vector $a = c_1 - c_2$ points along the C=C axis and the vector $n = (c_1 - r) \times (c_1 - r')$ is normal to the (C,R,R′) plane; the pyramidalization angle Φ is thus given by $|90 - \psi|$, where $\cos \psi = a \cdot n/(|a| \cdot |n|)$.

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Results and Discussion

Syntheses

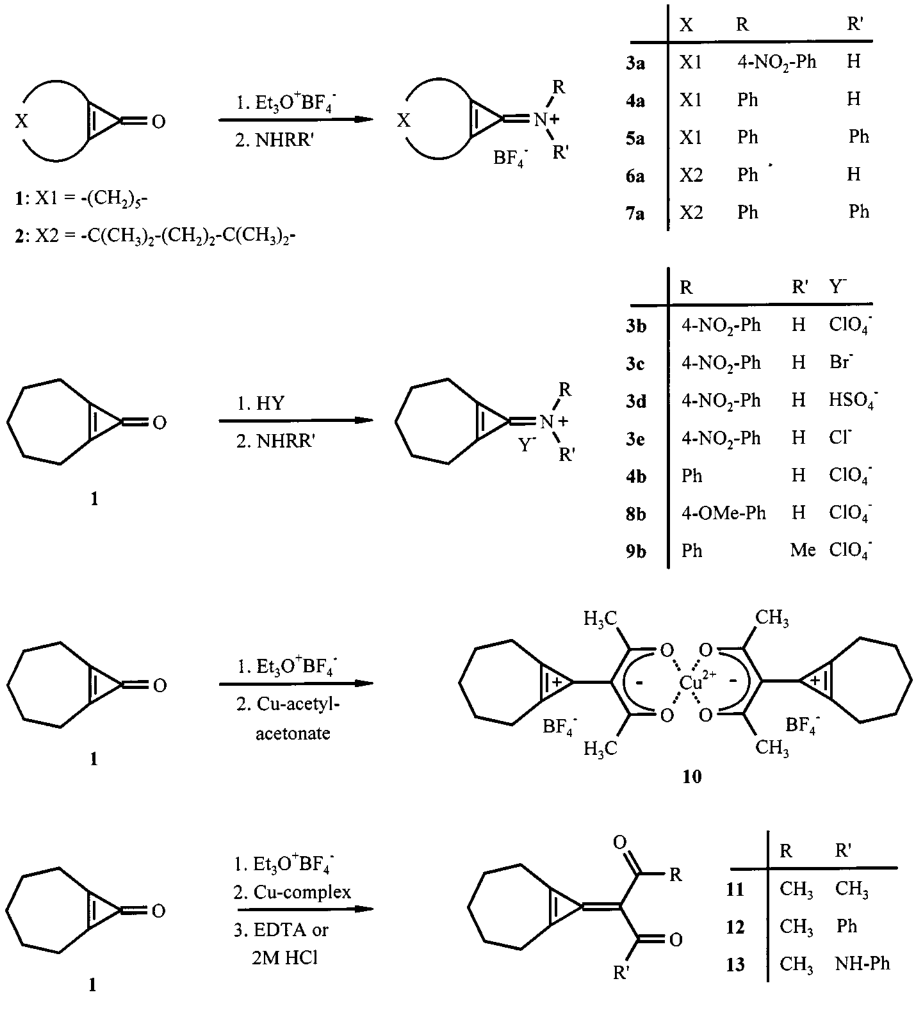
Starting from the known cyclopropenones **1** and **2**,[19,20] we obtained the ammonium tetrafluoroborates **3a**[21] and **4a**−**7a** by treatment with triethyloxonium tetrafluoroborate $Et_3O^+BF_4^-$, followed by primary or secondary amines.[22] The ammonium salts **3b**−**e**, **4b**, **8b**, and **9b** were synthesized in the same way, using mineral acids ($HClO_4$, HBr, H_2SO_4, HCl) instead of $Et_3O^+BF_4^-$.[22a,23] The ketone **1** was converted with $Et_3O^+BF_4^-$ and cupric acetylacetonate into compound **10**. Treatment of **10** with EDTA resulted in dione **11**; the diones **12** and **13** were synthesized in the same way except that the corresponding cupric complexes were used instead of cupric acetylacetonate, and hydrochloric acid instead of EDTA[24] (Scheme 2).

The cyclopropenones **1** and **2** dimerize in a thermal reaction to give the spirolactones **14** and **15**, respectively (Scheme 3).[25] Both were previously described in former publications;[26,27] however, the crystal structure of **15** has not been reported.

On trying to reduce the carbonyl group[28] of the lactone **15**, we obtained product **16** (Scheme 4), the molecular structure of which was proven by X-ray analysis.

Crystal Structures

X-ray structure analyses were performed for the cyclopropenone **1**, the ammonium salts **3a**, **4b**, **5a**, and **7a**, the

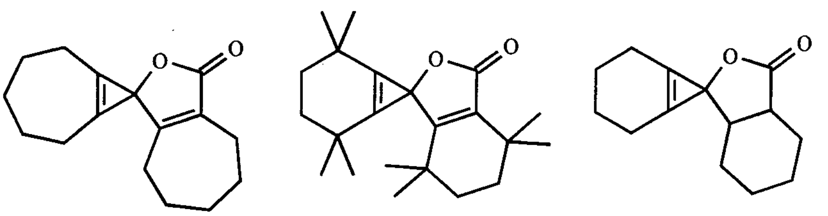


	X	R	R'
3a	X1	4-NO_2-Ph	H
4a	X1	Ph	H
5a	X1	Ph	Ph
6a	X2	Ph	H
7a	X2	Ph	Ph

	R	R'	Y^-
3b	4-NO_2-Ph	H	ClO_4^-
3c	4-NO_2-Ph	H	Br^-
3d	4-NO_2-Ph	H	HSO_4^-
3e	4-NO_2-Ph	H	Cl^-
4b	Ph	H	ClO_4^-
8b	4-OMe-Ph	H	ClO_4^-
9b	Ph	Me	ClO_4^-

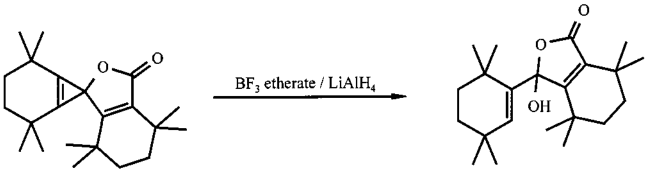
	R	R'
11	CH_3	CH_3
12	CH_3	Ph
13	CH_3	NH-Ph

Scheme 2. The syntheses of compounds **3**−**13**



14 **15** **M15**

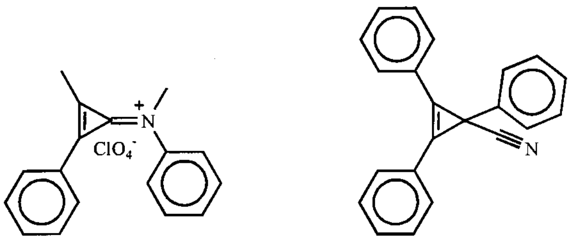
Scheme 3. The structural formulae of spirolactones **14** and **15** and model **M15**



15 **16**

Scheme 4. The synthesis of semiacetal **16**

cupric complex **10**, the diones **11** and **13**, the spirolactone **15**, and the hemiacetal **16**. The structure[12] of the spirolactone **14** was redetermined under our experimental conditions to be comparable with the structure determination of the other compounds. In addition, the structures of the cyclopropene compounds **17** and **18**[29] were determined for comparative purposes (Scheme 5).



17 **18**

Scheme 5. The structural formulae of the monocyclic cyclopropenes **17** and **18**

Structural data can be found in the Cambridge Crystallographic Database.[36] Figure 2 shows the crystal structures of cyclopropenone **1**, ammonium salts **4b**, **5a**, and **7a**, cupric complex **10**, diones **11** and **13**, and lactone **15**.

Table 1 gives selected bond lengths A and B, the bond angles χ (Figure 3), and the pyramidalization angles Φ of the bridgehead atoms, discussed below. In principle, the "right" and "left" Φ angles of the bridgehead atoms could differ significantly, but in almost all cases both angles are equal within the accuracy of our X-ray analyses. Because of its strongly disordered crystal structure, tetrafluoroborate **3a** was not used in the discussion of the deformations and so served only for proving the molecular structure of compound **3a**.

Theoretical Investigations

Our experimental findings were complemented by theoretical studies of various model systems (Scheme 6). Moreover, the theoretical findings allowed us to assess the influence of packing effects and counter-ions on the geometrical structures in the solid state. All geometrical data discussed in this communication were obtained at the Hartree–Fock (HF) self-consistent field (SCF) level of theory. We are primarily interested in the equilibrium geometries of closed-shell molecules, and thus the electron-correlation effects on the relevant observables were expected to be small. However, it was not clear, a priori, whether extended basis sets would be needed for an accurate description of pyramidalization angles in the strongly strained systems considered in this context.[31] Consequently, in the **M-73.O** model (the numbers reflect ring sizes and the final letter indicates the substituent) the dependence of the pyramidalization angle on the number of polarization functions in the basis set was examined. Our results are displayed in Table 2.

Somewhat surprisingly, the standard 6-31G(d) basis set turned out to be sufficiently flexible. There were virtually no differences between the 6-31G(d) value for the pyramidalization angle and the values obtained with the 6-31G(2d,p) and 6-31G(2df,p) basis sets. In contrast, the 3-21G basis was too small to provide accurate results, but our investigation of the other model species showed that it was capable of reproducing the trends in the pyramidalization angles.

The investigation of the first six model compounds **M-73.X** and **M-63.X** (X = C, O, N) focused on the influence on pyramidalization of the charge differences at the bridgehead atoms. The geometrical parameters obtained at the SCF/6-31G(d) level are collected in Table 3. Pyramidalization increases, as expected, with increasing negative partial charge on the bridgehead carbon atoms (Figure 4). These findings are discussed in the next section.

In the model studies described above, all substituents were replaced by hydrogen atoms. To check the validity of this approach, the geometries of the cations of compounds **4b** and **5a** (**M4b** and **M5a**), together with those of the lactones **14** and **M15**, were optimized using the 3-21G basis set (Table 4).

Comparison of the theoretical results for **M4b** and **M5a** with our results for the **M73.N** models shows that the replacement by H atoms has only a minor effect. Moreover, the comparison with the experimental results is quite satisfying both for the neutral compounds **14** and **M15** and for the ionic compound **M4b**. Experimentally determined and theoretically calculated bond lengths and angles are in agreement within 1%. The reason for the distinct deviation between the "real" and the model system of **5a** is discussed in the next section.

Finally, the energetic changes associated with an adiabatic distortion of the pyramidalization angle of four cyclopropene species (models **M3.X**, Scheme 6) were studied at the SCF/6-31G(d) level of theory. To this end, both torsion angles τ ($H^{1a}-C^{1a} = C^{1b}-C^2$ and $H^{1b}-C^{1b} = C^{1a}-C^2$; Figure 5) were fixed at a given value between 180 and 160° and all other bond lengths and angles were reoptimized. By these means, a "minimal energy pyramidalization pathway" was obtained (Figure 6).

For all systems considered, the amount of energy needed to enforce a significant degree of pyramidalization was found to be much smaller than the typical molecular strain

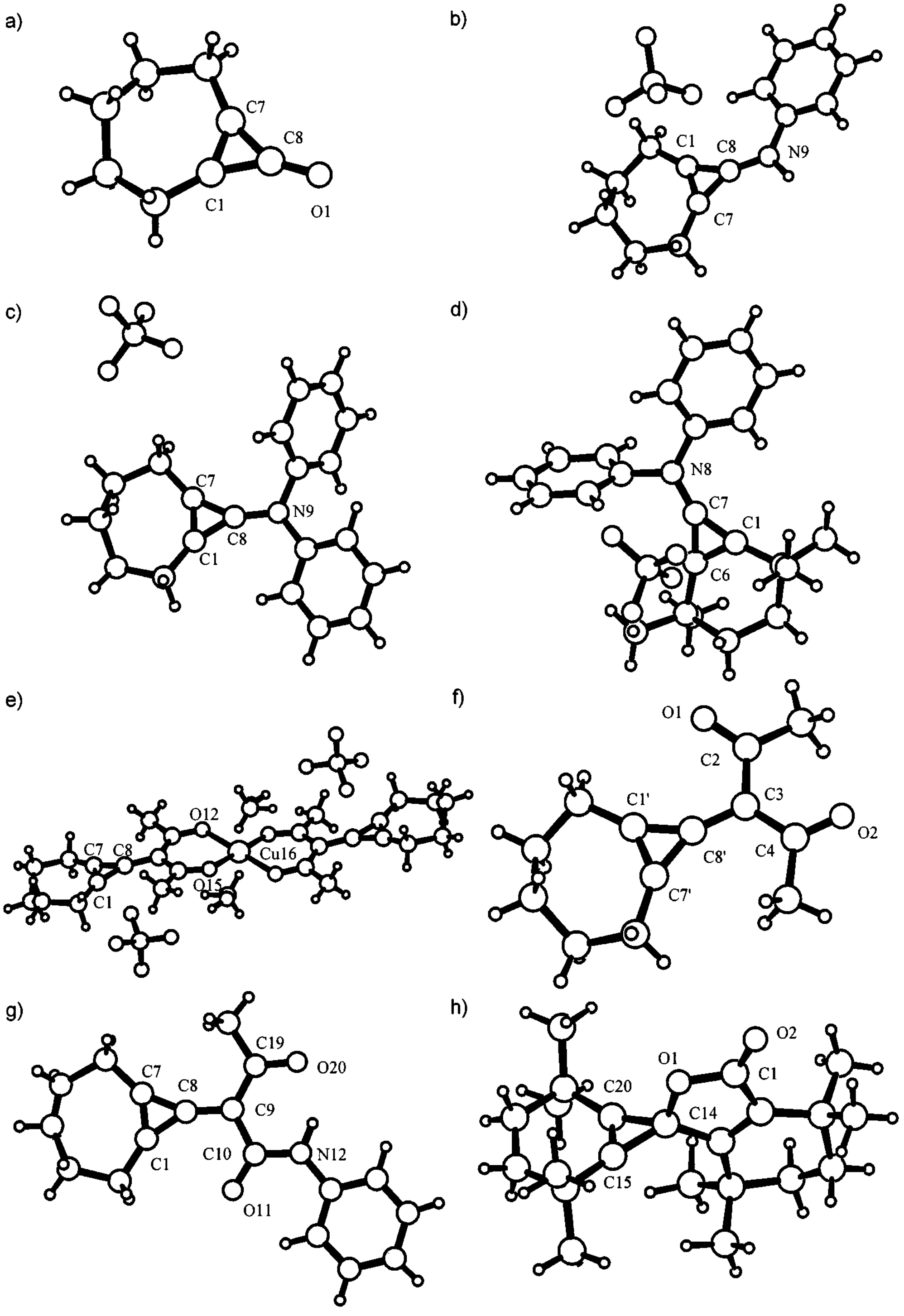


Figure 2. Molecular structures[30] of compounds a) **1**, b) **4b**, c) **5a**, d) **7a**, e) **10**, f) **11**, g) **13**, h) **15**

energies associated with Bayer and Pitzer strain.[33] For example, a pyramidalization angle of $\Phi = 16°$ (this value corresponds with $\tau = 160°$ for the investigated model **M-3.N**) introduced a strain energy of about 8.2 kJ/mol. Since these energies are quite small, a tradeoff between different sources of strain will most probably favor a large pyramidalization angle. These findings agree with the results of corresponding investigations on norbornene and several of its derivatives.[34] However, even if there is a considerable amount of strain energy in some other part of the molecule, a significant pyramidalization of a double bond might only be expected if the associated distortion allowed the release of this strain. We come back to this point in the next section.

Ab initio calculations: All theoretical investigations were carried out with the programs Spartan[39] or Gaussian.[40]

Table 1. Selected bond lengths and angles and the pyramidalization angles of the cyclopropenes **1**, **4b**, **5a**, **7a**, **10**, **11**, **13**, **14**, **15**, **17**, and **18**; A, B, and χ are defined in Figure 3; Φ is defined in Figure 1

Compound	A [Å]	B [Å] average	χ [°] average	Φ [°]	Φ [°] average
1	1.342(2)	1.416(3)	138.7(2)	7.4(5)/8.5(5)	7.9(5)
4b	1.331(3)	1.379(3)	140.2(2)	0.5(4)/0.8(4)	0.7(4)
5a	1.333(4)	1.384(4)	140.0(3)	9.2(5)/10.1(5)	9.7(5)
7a	1.333(4)	1.383(4)	129.6(3)	4.2(4)/16.0(4)	10.1(4)
10	1.326(3)	1.385(2)	140.3(2)	6.1(2)/4.1(2)	5.1(2)
11	1.324(2)	1.404(2)	140.1(1)	1.3(3)/0.8(3)	1.1(3)
13	1.320(3)	1.395(3)	140.4(2)	5.0(5)/4.3(5)	4.7(5)
14	1.288(2)	1.485(2)	140.8(2)	14.2(3)/14.7(3)	14.5(3)
15	1.277(5)	1.489(5)	130.4(3)	31.6(5)/30.2(5)	30.9(5)
17	1.349(3)	1.387(4)	148.5(2)	1.2(5)/3.2(5)	2.2(5)
18	1.299(3)	1.523(3)	155.6(2)	2.6(6)/2.2(6)	2.4(6)

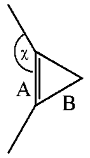
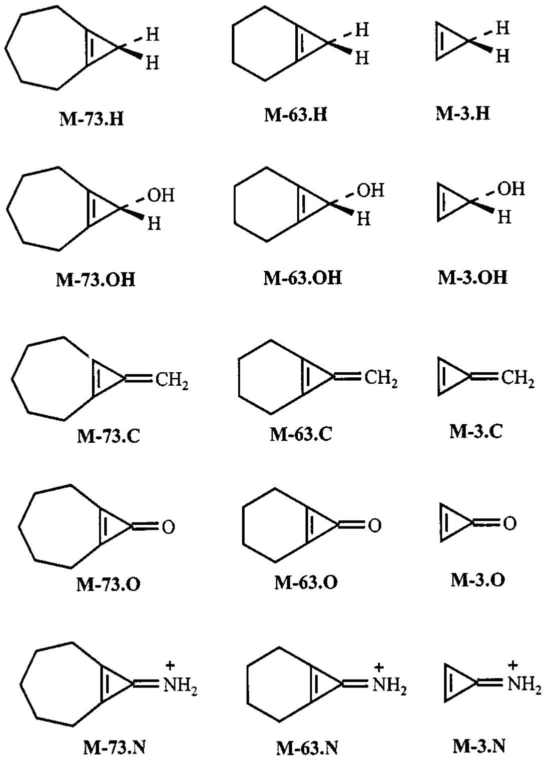


Figure 3. Definitions of bond lengths A and B and bond angle χ



Scheme 6. The structural formulae of the models used in geometry optimizations

Table 2. Results of different geometry optimizations on model **M−73.O**

Model	A [Å]	B [Å] average	Φ [°] average	Basis set
M-73.O	1.332	1.430	2.9	3−21G
M-73.O	1.329	1.413	4.3	6−31G(d)
M-73.O	1.329	1.415	4.3	6−31G(2d,p)
M-73.O	1.328	1.412	4.3	6−31G(2df,p)

Table 3. Geometrical parameters of the model systems (Scheme 6) at the SCF/6-31G(d) level of theory; the bond lengths A and B are defined in Figure 3 and given in Å, the pyramidalization angle Φ is defined in Figure 1 and given in °

Model	A [Å]	B [Å]	Φ [°]	χ [°]
M-73.H	1.275	1.498	11.7	140.9
M-73.OH	1.287	1.470	17.2	140.2
M-73.C	1.302	1.429	7.6	140.1
M-73.O	1.329	1.413	4.3	138.6
M-73.N	1.334	1.371	0.9	139.9
M-63.H	1.272	1.500	1.6	129.5
M-63.OH	1.278	1.474	41.4	128.7
M-63.C	1.298	1.431	1.02	128.7
M-63.O	1.324	1.415	1.01	127.7
M-63.N	1.331	1.370	0.52	128.4
M-3.H	1.275	1.495	0.0	150.2
M-3.OH	1.287	1.467	4.9	148.9
M-3.C	1.302	1.428	0.0	148.4
M-3.O	1.327	1.412	0.0	145.2
M-3.N	1.327	1.374	0.0	146.7

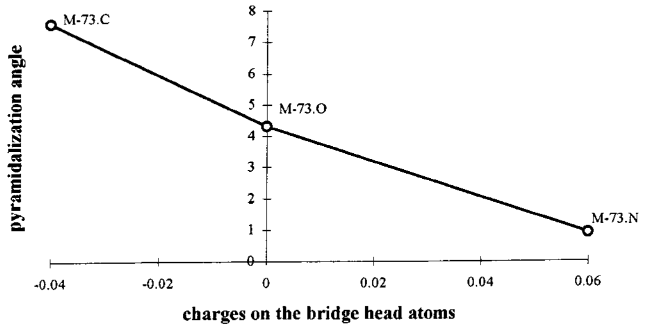


Figure 4. The correlation between the pyramidalization angles and the charges on the bridgehead atoms in the **M−73** models, derived from a Mulliken population analysis[32]

Table 4. Results of the geometry optimizations on the model compounds **M4b**, **M5a**, **14**, and **15** at the SCF/3-21G level of theory

Model	A [Å]	B [Å] average	χ [°] average	Φ [°] average
M4b	1.336	1.392	140.4	1.1
M5a	1.335	1.393	140.4	1.1
14	1.289	1.487	141.1	12.9
M15	1.286	1.492	129.5	26.0

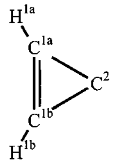


Figure 5. The definition of the torsion angles τ: $H^{1a}-C^{1a}-C^{1b}-H^{1b}$

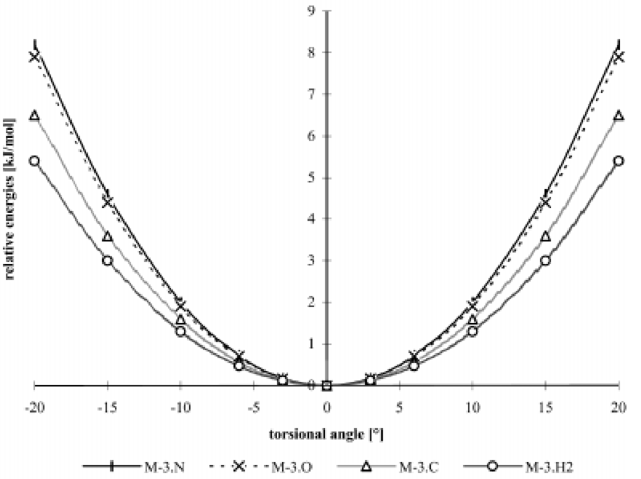


Figure 6. The relative energies of the models **M-3.H2**, **M-3.C**, **M-3.O**, and **M-3.N** and dependence of the torsion angle at the carbon atoms of the cyclopropene double bond

Discussion

For a discussion of pyramidalization, we distinguish between the bicyclic cyclopropenes **14** and **15** and the bicyclic cyclopropenylidenes **1**, **4b**, **5a**, **7a**, **10**, **11**, and **13**. The structural results for **17** and **18** served for comparison.

The two cyclopropene derivatives **14** and **15** show strong pyramidalization of 14.5° and 30.9°, respectively. Pronounced distortions of the same order of magnitude are also found in the model calculations for **14** and **M15** (Table 4) and, thus, packing effects should have virtually no influence on this geometrical parameter. To analyze the observed trends, we performed ab initio geometry optimizations for the simpler cyclopropene derivatives **M-63.H**, **M-63.OH**, **M-73.H**, and **M-73.OH** (Scheme 6, Table 3). For the six- and seven-membered ring model systems, twist and chair conformations, respectively, were found, in analogy to the minimum energy conformations found for the monocyclic cyclohexene and cycloheptene species.[41] Let us note that these conformations are prototypical for our experimentally determined structures. Our model calculations clearly indicate that the six- and seven-membered ring systems, despite their superficial similarity, behave quite differently. While the double bond in **M-63.H** is almost planar (Φ = 1.6°), we found the analogous seven-membered ring compound **M-73.H** to be substantially pyramidalized (Φ = 11.7°). The chair conformation of the seven-membered ring in **M-73.H** is obviously sufficiently flexible to allow a reduction of ring strain by pyramidalization of the bridging double bond, whereas pyramidalization cannot significantly reduce the strain in **M-63.H**. We attribute this behavior to the twist conformation (local C_2 symmetry) of the six-membered ring. The C_2 symmetry of the bicyclic subsystem is necessarily broken by a pyramidalizing distortion and, loosely speaking, any ring strain released at the right hand side of the double bond will increase the strain at the left hand side. Thus, the strain in the six-membered ring should depend only weakly on the pyramidalization angle Φ.

This situation changes dramatically when an OH group is attached at the three-membered ring (see Scheme 6). On going from **M-73.H** to **M-73.OH**, the pyramidalization is increased by 5.4° to 17.2°, and a huge distortion of Φ = 41.4° is found for **M-63.OH**. These large pyramidalizations can be rationalized in terms of a π/oxygen lone pair repulsion as follows. Let us start with a supposedly unpyramidalized cyclopropenol system (**M-X3.OH**); i.e., with sp^2-hybridized bridgehead atoms. Then, the "closed-shell" repulsion between the occupied π-orbital of the double bond and the oxygen lone pairs will favor rehybridization of the bridgehead carbon atoms towards sp^3 (i.e., pyramidalization), since electron density can be moved by these means to the molecular plane opposite to the oxygen atom. This effect is, in principle, independent of any annulated ring, and even cyclopropenol **M-3.OH** exhibits a pronounced pyramidalization of Φ = 4.9°, where the H atoms are bent towards the OH side. However, the annulated ring will of course have a strong influence on the "equilibrium" pyramidalization, since ring strain and π/lone pair repulsion have to be balanced with each other. Thus, the observed pyramidalizations of the lactones **14** and **15** can be thought of as arising essentially from two effects. Firstly, the double bond will pyramidalize if ring strain can be reduced in this way. This effect is rather weak for the six-membered ring compounds, but substantial for the seven-membered ring species. Secondly, there is the repulsion between lactone oxygen lone pairs and the occupied π-orbital, which can be reduced by a pyramidalizing distortion. This factor increases the distortions in **M-73.OH** and **14**, relative to **M-73.H**, and is the dominant source of pyramidalization of the six-membered ring systems **15**, **M15**, and **M-63.OH**. The somewhat smaller degrees of pyramidalization in the lactones **15** and **14**, in comparison with the corresponding model compounds **M-63.OH** and **M-73.OH**, can be understood in terms of a reduced electron density at the lactone oxygen atom, due to the vicinal carbonyl group.

Let us now turn to the cyclopropenylidenes for which the electronic influence on pyramidalization has been studied. The ab initio calculations for the model compounds **M-63** and **M-73** (Scheme 6) show that, within the bicyclooctene group (**M-73.N**, Φ = 0.9°; **M-73.O**, Φ = 4.3°; **M-73.C**, Φ = 7.6°) and the bicyloheptene group (**M-63.N**, Φ = 0.52°; **M-63.O**, Φ = 1.01°; **M-63.C**, Φ = 1.02°), pyramidalization at the bridgehead atoms increases from the ammonium ions (**M-63.N**, **M-73.N**) through the cyclopropenones (**M-63.O**, **M-73.O**) to the methylenecyclopropenes (**M-63.C**, **M-73.C**; Table 3). In the same direction, we observe a shortening of the cyclopropene double bonds and a lengthening of both cyclopropene single bonds (Table 3). This observation conforms to a decrease in cyclopropenylium character and an increase in electron density at the bridgehead atoms. The same tendencies in electron density can be derived from a Mulliken population analysis (Figure 4).[32] Within the groups **M-63** and **M-73**, pyramidalization increases with increasing electron density at the bridgehead atoms. Consequently, the pyramidalization in cyclopropenylidenes is less pronounced than in cyclopropenes such as **14** or **15**, which clearly show a considerably reduced cyclopropenylium character.

Surprisingly, the bicyclooctenes (**M-73**) are more strongly pyramidalized than the bicycloheptenes (**M-63**), even though the ring strain increases from the bicyclooctene to the bicycloheptene. This trend can again be explained in terms of the different conformations of the six- (twist) and seven-membered (chair) rings (see discussion above). The small ring size of the cyclohexene moiety prevents large twisting deformations, and therefore pyramidalization at the bridgehead atoms cannot reduce the ring strain. In contrast, the chair conformation of the cycloheptene moiety allows pyramidalization without conformational hindrance.

Let us return to the trends regarding the electron density at the bridgehead atoms. The theoretical considerations are supported by the experimental results. If we assume that the electron-density distributions of **1**, **4b**, **5a**, **7a**, **10**, **11**, and **13** correlate with the observed bond lengths in the cyclopropene systems (Table 1), we can classify the investigated compounds as follows. According to the shortening of bond type B, the electron density at the bridgehead atoms must decrease from the ketone **1**, through the diones **13** and **11**, to the ammonium salts **4b**, **5a**, and **7a**, and the cupric complex **10**. As expected, the cyclopropenone **1** [$\Phi = 7.9(5)°$] shows the strongest pyramidalization in the cyclopropenylidene group, and the diones **13** [$\Phi = 4.7(5)°$] and **11** [$\Phi = 1.1(3)°$] exhibit smaller pyramidalizations. In view of the theoretical results, the remaining cyclopropenylidenes should be essentially planar (Table 3 and Table 4), but only the perchlorate **4b** [$\Phi = 0.7(4)°$] fulfills this expectation. In contrast, the tetrafluoroborates **5a** [$\Phi = 9.7(5)°$], **7a** [$\Phi = 10.1(4)°$], and **10** [$\Phi = 5.1(2)°$] all show distinct pyramidalization at their bridgehead atoms. However, the crystal structures of these three compounds show that the deformations are probably the results of intermolecular contacts. In the three crystals of the salts **5a**, **7a**, and **10**, short distances are observed between tetrafluoroborate fluorine atoms and the bridgehead atoms of the cations, and this interaction could give rise to the detected pyramidalizations. Moreover, the investigation of the **M.3** models (Figure 6) clearly shows that even minor effects can lead to significant deformations.

Conclusions

We have investigated bicyclo[4.1.0]hept-1(6)-ene and bicyclo[5.1.0]oct-1(7)-ene systems by X-ray diffraction and ab initio methods. The syntheses of **3b−3e**, **4a**, **4b**, **6a**,**7a**, **8b**, **9b**, **12**, **13**, and **16** have been described, and the structures of **1**, **3a**, **4b**, **5a**, **7a**, **10**, **11**, and **13−16** have been determined from X-ray analyses. To complement these experimental data, several model compounds have been studied theoretically.

For the cyclopropenes **14** and **15**, a substantial pyramidalization has been observed, and the six-membered ring species was considerably more strongly deformed than the seven-membered one. Since the electronic influences in these species should be almost equal, the dominating difference must be the ring size, and one could be tempted to conclude that the larger ring strain in **15** is responsible for the larger pyramidalization. However, our analysis with the aid of the model compounds **M-3.OH**, **M-63.H**, **M-63.OH**, **M-73.H**, and **M-73.OH** clearly shows that the decisive factor is not simply ring size, but conformation. While the chair conformation of the annealed seven-membered ring allows an effective reduction of ring strain by pyramidalization of the double bond, the twist conformation of the six-membered ring can profit only very little from a pyramidalizing distortion. A second factor favoring a strong degree of pyramidalization in **14** and **15** is the repulsion between the occupied π-bond and the oxygen lone pairs. This effect adds to the pyramidalization stemming from ring strain in **14**, and is the dominant source of deformation in **15**.

For the cyclopropenylidenes, we have studied the electronic influence on pyramidalization. Let us note that the pyramidalizing deformation is ultimately caused by steric effects, but that its magnitude strongly depends on electronic factors. Essentially, a large degree of pyramidalization is favored by a weak cyclopropenylium character; i.e., by a large A/B bond length difference or by an increased charge density at the bridgehead atoms. In other words, the stronger the conjugation of the bridging with the exocyclic double bond, the less likely is a substantial degree of pyramidalization. Thus, cyclopropenylidenes should, in general, exhibit smaller deformations than analogous cyclopropene systems. However, our results for the **M-3.X** model species clearly show that a pyramidalizing distortion is a soft mechanism (Figure 5 and Figure 6) and, thus, “environmental” influences such as the interaction with a counter-ion (**5a**, **7a**, **10a**) can also have a pronounced influence.

Experimental Section

Melting points: Büchi Melting Point B-540 (Switzerland), open capillary tubes. − IR: Bruker IFS 66 with a Bruker CS Computer. − UV/Vis: HP 8452A (Diode Array). − NMR: 200 MHz ^{1}H NMR: Bruker AC 200; 300 MHz ^{1}H NMR and 75 MHz ^{13}C NMR: Bruker AC 300 (solvent as internal standard). − MS: Vacuum Generators, VG MICROMASS ZAB-2F Sectorfield-MS (EI); Jeol, JMS-700 Sectorfield-MS (FAB+, FD+). − EA: Heraeus CHN−O Rapid.

General Procedure for the Preparation of the Salts 3b−e, 4b, 8b, and 9b: A primary or secondary amine (4.1 mmol) was dissolved in 10 mL of dry ethanol in a 250-mL flask. An aqueous solution of mineral acid (8.2 mmol), and then a solution of ketone **1** (0.50 g, 4.1 mmol) in dry ethanol (10 mL), was added. In most cases, the raw products precipitated after stirring for 30 min; otherwise the solution was heated to reflux for 30 min. Afterwards, the products could in all cases be precipitated by addition of diethyl ether (150 mL). The crude products were purified either by recrystallization from ethanol/acetonitrile (10:1) or by stirring in diethyl ether.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(4-nitrophenyl)ammonium Perchlorate (3b): 4-Nitroaniline (0.57 g, 4.1 mmol), aq. perchloric acid (35%, 2.34 g, 8.2 mmol). After recrystallization, 0.36 g of **3b** (25%) was obtained, as light yellowish crystals, m.p. 230−233 °C under decomposition. − IR (KBr): $\tilde{\nu}$ = 3219 cm^{-1}, 2937 (CH), 1911 (C=N$^+$), 1602, 1552, 1516 (C=C), 1344 (N=O), 1105 (ClO). − UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 198 nm (3.8), 216 (3.7), 292 (3.7), 346 (2.9). − ^{1}H NMR (200 MHz, [D$_6$]acetone): δ = 1.93−2.23 (m, 6 H, CH$_2$), 3.09−3.15 [t, *J* = 6.3 Hz, 2 H, CH$_2$], 3.33−3.40 [t, *J* = 6.2 Hz, 2 H, CH$_2$], 7.70−7.78 [d, *J* = 9.4 Hz, 2 H, aromatic H], 8.36−8.44 [d, *J* = 9.4 Hz, 2 H, aromatic H], 11.63 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]acetone): δ = 27.3, 27.4, 28.2, 29.8, 29.9 (5 C, CH$_2$), 119.7, 126.5 (4 C, aromatic C), 143.3, 146.0, 146.5, 156.7, 157.1 (5 C, quaternary C). − MS (FD+); *m*/*z* (%): 585 (5) [M$^+$ + C$_{14}$H$_{15}$N$_2$O$_2$], 243 (100) [M$^+$ − ClO$_4$]. − C$_{14}$H$_{15}$ClN$_2$O$_6$ (342.1): calcd. C 49.06, H 4.42, N 8.17; found C 48.81, H 4.27, N 8.12.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(4-nitrophenyl)ammonium Bromide (3c): 4-Nitroaniline (0.57 g, 4.1 mmol), aq. hydrobromic acid (35%, 1.87 g, 8.2 mmol). Stirring of the crude product with diethyl ether gave 0.58 g of **3c** (44%), yellowish crystals, m.p. 234−244 °C with decomposition. − IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1} (CH), 2715 (=N$^+$−H), 1912 (C=N$^+$), 1602, 1562, 1512 (C=C), 1343 (N=O). − UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 200 nm (4.3), 218 (4.2), 296 (4.0), 350 (3.3). − ^{1}H NMR (CDCl$_3$): δ = 1.99−2.18 (m, 6 H, CH$_2$); 3.15−3.19 [t, *J* = 5.9 Hz, 4 H, CH$_2$], 7.59−7.62 [d, *J* = 9.0 Hz, 2 H, aromatic H], 8.23−8.26 [d, *J* = 9.0 Hz, 2 H, aromatic H], 14.01 (s, 1 H, NH). − MS (FD+); *m*/*z* (%): 484 (13) [M$^+$ − Br + C$_{14}$H$_{13}$N$_2$O$_2$], 243 (47) [M$^+$ − Br], 242 (100) [M$^+$ − HBr]. − C$_{14}$H$_{15}$BrN$_2$O$_2$ (322.0): calcd. C 52.17, H 4.69, N 8.70, Br 24.51; found C 51.95, H 4.77, N 8.59, Br 24.68.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(4-nitrophenyl)ammonium Hydrogen Sulfate (3d): 4-Nitroaniline (0.57 g, 4.1 mmol), aq. sulfuric acid (75%, 1.07 g, 8.2 mmol). Stirring of the crude product with diethyl ether gave 0.66 g of **3d** (42%), as a light yellowish, crystalline solid, m.p. 142−146 °C with decomposition. − IR (KBr): $\tilde{\nu}$ = 2936 cm^{-1} (CH), 2719 (=N$^+$−H), 1911 (C=N$^+$), 1601, 1561, 1513 (C=C), 1342 (N=O). − MS (FD+); *m*/*z* (%): 484 (13) [M$^+$ − HSO$_4$ + C$_{14}$H$_{13}$N$_2$O$_2$], 243 (30) [M$^+$ − HSO$_4$], 242 (100) [M$^+$ − H$_2$SO$_4$]. − C$_{14}$H$_{16}$N$_2$O$_6$S · 0.5 C$_2$H$_5$OH (363.1): calcd. C 49.58, H 5.27, N 7.71, S 8.82; found C 49.59, H 5.23, N 7.84, S 8.82.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(4-nitrophenyl)ammonium Chloride (3e): 4-Nitroaniline (0.57 g, 4.1 mmol), aq. hydrochloric acid (35%, 0.84 g, 8.2 mmol). After recrystallization, 0.50 g of **3e** (44%) was obtained, as a yellow, crystalline solid, m.p. 204−208 °C with decomposition. − IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (CH), 2701, 2509 (=N$^+$−H), 1912 (C=N$^+$), 1603, 1566, 1509 (C=C), 1341 (N=O). − ^{1}H NMR (CDCl$_3$): δ = 1.98−2.32 (m, 6 H, CH$_2$), 3.11 (m, 2 H, CH$_2$), 3.19 (m, 2 H, CH$_2$), 7.61−7.64 [d, *J* = 8.9 Hz, 2 H, aromatic H], 8.21−8.23 [d, *J* = 8.7 Hz, 2 H, aromatic H], 14.85 (s, 1 H, NH). − MS (FD+); *m*/*z* (%): 276 (6) [M$^+$ − 2 H], 138 (100) [M$^+$ − C$_8$H$_9$]. − C$_{14}$H$_{15}$ClN$_2$O$_2$ (278.1): calcd. C 60.41, H 5.44, N 10.07; found C 59.62, H 5.51, N 9.96.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(phenyl)ammonium Perchlorate (4b): Aniline (0.38 g, 4.1 mmol), aq. perchloric acid (35%, 2.34 g, 8.2 mmol). Recrystallization of the crude product gave 0.16 g of **4b** (13%), as a white, glittering, plate-form solid, m.p. 223−226 °C. − IR (KBr): $\tilde{\nu}$ = 3242 cm^{-1}, 2939 (CH), 1912 (C=N$^+$), 1603, 1555, 1495 (C=C), 1111 (ClO). − UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 200 nm (4.5), 238 (4.3), 270 (3.4), 278 (3.2). − ^{1}H NMR ([D$_6$]acetone): δ = 1.94−2.03 (m, 2 H, CH$_2$), 2.08−2.22 (m, 4 H, CH$_2$), 3.07−3.13 [t, *J* = 6.1 Hz, 2 H, CH$_2$], 3.27−3.32 [t, *J* = 6.0 Hz, 2 H, CH$_2$], 7.33−7.39 (m, 1 H, aromatic H), 7.48−7.57 (m, 4 H, aromatic H), 11.20 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]acetone): δ = 27.2, 27.4, 28.0, 29.9, 30.1 (5 C, CH$_2$), 119.0, 127.3, 130.9 (5 C, aromatic C), 138.1, 145.3, 155.4 (4 C, quaternary C). − MS (FAB+); *m*/*z* (%): 495 (8) [M$^+$ − ClO$_4$ + C$_{14}$H$_{16}$N], 198 (100) [M$^+$ − ClO$_4$]. − C$_{14}$H$_{16}$ClNO$_4$ (297.1): calcd. C 56.48, H 5.42, N 4.70, Cl 11.91; found C 56.39, H 5.32 N 4.61 Cl 11.96.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(4-methoxyphenyl)ammonium Perchlorate (8b): 4-Methoxyaniline (0.50 g, 4.1 mmol), aq. perchloric acid (35%, 2.34 g, 8.2 mmol). Recrystallization of the crude product gave 0.16 g of **8b** (12%), as a light gray, glittering, plate-form solid, m.p. 214−215 °C. − IR (KBr): $\tilde{\nu}$ = 3239 cm^{-1}, 2936 (CH), 1916 (C=N$^+$), 1610, 1560, 1513 (C=C), 1252 (C−O−C), 1102 (ClO). − UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 196 nm (4.4), 250 (4.2), 286 (3.5). − ^{1}H NMR ([D$_6$]acetone): δ = 1.97−2.18 (m, 6 H, CH$_2$), 3.05−3.07 [t, *J* = 6.1 Hz, 2 H, CH$_2$], 3.22−3.27 [t, *J* = 6.2 Hz, 2 H, CH$_2$], 3.84 (s, 3 H, CH$_3$), 7.06−7.10 [d, *J* = 8.9 Hz, 2 H, aromatic H], 7.42−7.45 [d, *J* = 9.2 Hz, 2 H, aromatic H], 11.06 (s, 1 H, NH). − ^{13}C NMR ([D$_6$]acetone): δ = 27.2, 27.4, 27.8, 29.9, 30.1 (5 C, CH$_2$), 55.9 (CH$_3$), 116.0, 120.7 (4 C, aromatic C), 131.1, 145.0, 154.6, 154.8, 159.2 (5 C, quaternary C). − MS (FD+); *m*/*z* (%): 555 (56) [M$^+$ + C$_{15}$H$_{18}$NO], 228 (100) [M$^+$ − ClO$_4$]. − C$_{15}$H$_{18}$ClNO$_5$ (327.1): calcd. C 55.03, H 5.55, N 4.28, Cl 10.69; found C 54.83, H 5.54 N 4.15, Cl 10.95.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(methyl)(phenyl)ammonium Perchlorate (9b): *N*-Methylaniline (0.44 g, 4.1 mmol), aq. perchloric acid (35%, 2.34 g, 8.2 mmol). Recrystallization of the crude product gave 0.16 g of **9b** (13%), as a white, crystalline solid, m.p. 122 °C. − IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (CH), 1903 (C=N$^+$), 1595, 1536, 1497 (C=C), 1091 (ClO). − UV/Vis (CH$_3$CN): λ_{max} (lg ε) = 200 nm (4.9), 236 (4.6), 270 (3.7). − ^{1}H NMR (CDCl$_3$): δ = 1.89−2.06 (m, 6 H, CH$_2$), 2.80−2.85 [t, *J* = 6.1 Hz, 2 H, CH$_2$], 3.07−3.11 [t, *J* = 6.1 Hz, 2 H, CH$_2$], 3.78 (s, 3 H, CH$_3$), 7.39−7.45 (m, 5 H, aromatic H). − ^{13}C NMR ([D$_6$]acetone): δ = 27.0, 27.3, 27.4, 29.9, 30.0 (5 C, CH$_2$), 42.1 (CH$_3$), 121.0, 128.4, 130.8 (5 C, aromatic C), 142.4, 148.5, 154.7, 155.7 (4 C, quaternary C). − MS (FD+); *m*/*z* (%): 523 (10) [M$^+$ + C$_{15}$H$_{18}$N], 212 (100) [M$^+$ − ClO$_4$]. − C$_{15}$H$_{18}$ClNO$_4$ (311.1): calcd. C 57.79, H 5.82, N 4.49, Cl 11.37; found C 57.50, H 5.83, N 4.39, Cl 11.23.

General Procedure for the Preparation of Compounds 4a and 5a: The reaction was carried out in a sealed flask under nitrogen. The cyclopropenone **1** (1 g, 8.2 mmol) was dissolved in dry dichloromethane (8.2 mL) and a solution of triethyloxonium tetrafluoroborate Et$_3$O$^+$BF$_4$$^-$ in dichloromethane (1 M, 9.2 mL, 9.2 mmol) was added. After stirring at room temperature for 20 min, a solution of a primary or secondary amine (9.0 mmol) was added slowly. The reaction mixture was stirred for a further 2 h. The products were isolated by removal of the solvent under reduced pressure and purified by recrystallization from methanol.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidene(phenyl)ammonium Tetrafluoroborate (4a): Aniline (0.84 g, 9.0 mmol). Recrystallization of the crude product gave 2.2 g of **4a** (84%), as colorless crystals, decomposition point 233−234 °C. − IR (KBr): $\tilde{\nu}$ = 3284 cm^{-1}, 2939 (CH), 1915 (C=N$^+$), 1602, 1556, 1495 (C=C), 1082 (BF). − UV/Vis (methanol): λ_{max} (lg ε) = 202 nm (4.2), 240 (4.1), 272 (3.2), 282 (3.0). − ^{1}H NMR ([D$_6$]acetone): δ = 1.91−2.17 (m, 6 H, CH$_2$), 3.02−3.06 [t, *J* = 6.2 Hz, 2 H, CH$_2$], 3.22−3.26 [t, *J* = 6.2 Hz, 2

H, CH_2], 7.32−7.54 (m, 5 H, aromatic H), 10.94 (s, 1 H, NH). − ^{13}C NMR ([D_6]acetone): δ = 27.0, 27.3, 27.9, 29.8, 30.0 (5 C, CH_2), 118.9, 127.2, 130.9 (5 C, aromatic C), 138.0, 145.2, 155.4, 155.4 (4 C, quaternary C). − MS (FAB+); *m/z* (%): 483.3 (4) [M^+ + $C_{14}H_{16}N$], 198.1 (100) [M^+ − BF_4]. − $C_{14}H_{16}BF_4N$ (285.1): calcd. C 58.89, H 5.66, N 4.91; found C 59.19, H 5.82.

Bicyclo[5.1.0]oct-1(7)-en-8-ylidenebis(phenyl)ammonium Tetrafluoroborate (5a): Diphenylamine (1.52 g, 9.0 mmol). Recrystallization of the crude product gave 2.7 g of **5a** (91%), as colorless crystals, m.p. 172 °C. − IR (KBr): ṽ = 2949 cm^{-1} (CH_2), 1901 ($C=N^+$), 1590, 1508, 1456 (C=C), 1054 (BF). − UV/Vis (methanol): λ_{max} (lg ε) = 206 nm (4.3), 236 (4.0), 278 (3.6). − ^1H NMR ($CDCl_3$): δ = 1.90−2.03 (m, 6 H, CH_2), 2.83−2.87 [t, *J* = 5.8 Hz, 4 H, CH_2], 7.36−7.43 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 26.1, 26.4, 28.9 (5 C, CH_2), 123.5, 128.6, 130.1 (10 C, aromatic C), 141.2, 147.2, 155.1 (5 C, quaternary C). − MS (FAB+); *m/z* (%): 635.3 (5) [M^+ + $C_{20}H_{20}N$], 274.2 (100) [M^+ − BF_4]. − $C_{20}H_{20}BF_4N$ (361.2): calcd. C 66.51, H 5.58, N 3.88; found C 66.77, H 5.58.

General Procedure for the Preparation of the Salts 6a and 7a: The reaction was carried out in an sealed flask under nitrogen. After dissolving ketone **2** in dry dichloromethane and cooling the reaction mixture to 0 °C, a 1 M solution of triethyloxonium tetrafluoroborate $Et_3O^+BF_4^-$ in dichloromethane was added. The reaction mixture was stirred for 30 min. A solution of the primary or secondary amine in dry dichloromethane was added dropwise over 15 min. After a reaction time of 3 h, the solvent was removed under reduced pressure and a few drops of acetone were added to dissolve the yellow-green residue. The crude product could be precipitated by adding a few drops of diethyl ether and cooling the mixture to −25 °C. It was purified by reprecipitating with acetone and diethyl ether.

2,2,5,5-Tetramethylbicyclo[4.1.0]hept-1(6)-en-7-ylidene(phenyl)ammonium Tetrafluoroborate (6a): Compound **2** (0.17 g, 1.04 mmol) in dry dichloromethane (2.5 mL), $Et_3O^+BF_4^-$ in dichloromethane (1.22 mL, 1.22 mmol), aniline (0.93 mg, 1.14 mmol) in dry dichloromethane (2 mL). Recrystallization of the crude product gave 0.72 g of **6a** (21%), as a white, glittering, plateform solid, decomposition point 190−191 °C. − IR (KBr): ṽ = 3245 cm^{-1}, 2937 (CH), 1889 ($C=N^+$), 1602, 1540, 1457 (C=C), 1084 (BF). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε): 242 nm (4.2), 272 (3.6), 282 (3.4). − ^1H NMR ($CDCl_3$): δ = 1.41 (s, 6 H, CH_3), 1.42 (s, 6 H, CH_3), 1.94 (s, 4 H, CH_2), 7.26−7.43 (m, 5 H, aromatic H), 10.77 (s, 1 H, NH). − ^{13}C NMR ([D_6]acetone): δ = 24.8, 25.3 (4 C, CH_3), 34.6, 35.0 (2 C, $C(CH_3)_2$), 37.4, 37.7 (2 C, CH_2), 118.3, 127.8, 131.0 (5 C, aromatic C), 137.4, 138.9, 161.4, 161.7 (4 C, quaternary C). − MS (HRFAB+); *m/z* (%): 327.1656 (14) [$M^+(^{11}B)$], 240.1663 (95) [M^+ − BF_4]. − $C_{17}H_{22}BF_4N$ (327.0): calcd. C 62.39, H 6.78, N 4.28; found C 61.65, H 6.83, N 4.21.

2,2,5,5-Tetramethylbicyclo[4.1.0]hept-1(6)-en-7-ylidenebis(phenyl)ammonium Tetrafluoroborate (7a): Compound **2** (0.14 g, 0.83 mmol) in dry dichloromethane (2 mL), $Et_3O^+BF_4^-$in dichloromethane (0.97 mL, 0.97 mmol), diphenylamine (0.15 g, 0.91 mmol) in dry dichloromethane (2 mL). Recrystallization of the crude product gave 0.06 g of **7a** (18%), as a white, powdery solid, easily charged electrostatically, decomposition point 231−238 °C. − IR (KBr): ṽ = 2967 cm^{-1}, 2931 (CH), 1885 ($C=N^+$), 1594, 1494, 1452 (C=C), 1057 (BF). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 234 nm (3.7), 238 (3.7), 268 (3.6). − ^1H NMR ($CDCl_3$): δ = 1.31 (s, 12 H, CH_3), 1.96 (s, 4 H, CH_2), 7.42−7.50 (m, 10 H, aromatic H). − ^{13}C NMR ([D_6]acetone): δ = 24.9 (4 C, CH_3), 34.9 (2 C, $C(CH_3)_2$), 37.5 (2 C, CH_2), 124.4, 129.9, 131.2 (10 C, aromatic C), 142.1, 142.7, 162.4 (5 C, quaternary C). − MS (HRFAB+); *m/z* (%): 719.5628 (1.3) [$M^+(^{11}B)$ + $C_{23}H_{26}N$], 316.2042 (100) [M^+ − BF_4]. − $C_{23}H_{26}BF_4N$ (403.0): calcd. C 68.49, H 6.50, N 3.47; found C 67.88, H 6.52, N 3.45.

General Procedure for the Preparation of the Cupric Complex 10 and the Diones 11, 12, and 13: The reaction was carried out in a sealed flask under nitrogen. To the ketone **1** dissolved in dry dichloromethane was added a 1 M solution of the triethyloxonium tetrafluoroborate $Et_3O^+BF_4^-$ in dichloromethane. After stirring the reaction mixture for 30 min, the cupric complex was added as a solid and the stirring was continued for 3 h. Next, half of the solvent was removed under reduced pressure. The cupric complex of ketone **1** precipitated and was isolated. The complex (**10**) was purified by recrystallization from methanol. To isolate the dione **11**, a solution of the crude cupric complex **10** in dichloromethane was treated with a saturated aq. EDTA solution. In order to isolate the diones **12** and **13**, the crude copper complexes were heated with a mixture of 2-propanol and 2 M hydrochloric acid (1:1). Afterwards, the reaction mixture was diluted with water and the products were extracted with dichloromethane. In both cases (the isolation of **11** as well as the isolation of **12** and **13**), the combined organic layers were washed with an aq. $NaHCO_3$ solution (5%) and water and dried with Na_2SO_4. The solvent was evaporated. The dark, oily crude products were purified either by column chromatography on silica gel (0.32−0.64 Å) with dichloromethane/diethyl ether (1:1) as eluent, or by heating to reflux in diethyl ether.

[3-{Bicyclo[5.1.0]oct-1(7)-en-8-ylidene}pentane-2,4-dionato]copper (10): Compound **1** (1.00 g, 8.2 mmol) in dry dichloromethane (16 mL), $Et_3O^+BF_4^-$ in dichloromethane (1 M, 8.6 mL, 8.6 mmol), cupric acetylacetonate (2.14 g, 8.2 mmol). The dark blue raw product was purified by recrystallization from methanol to afford 1.34 g of **10** (50%), as light blue crystals, decomposition point 260 °C. − IR (KBr): ṽ = 2938 cm^{-1} (CH), 1864 (C=C), 1612 (C=O), 1453, 1390 (CH), 1059 (BF). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 236 nm (4.3), 266 (4.7), 294 (4.4). − MS (HRFAB+); *m/z* (%): 560.1617 (7) [$M^+(^{65}Cu)$ − BF_4], 558.1616 (15) [$M^+(^{63}Cu)$ − BF_4], 471.1578 (9) [$M^+(^{63}Cu)$ − B_2F_8]. − $C_{26}H_{32}B_2CuF_8O_4 \cdot 2\ CH_3OH$ (709.4): calcd. C 47.36, H 5.68; found C 46.14, H 5.88.

3-{Bicyclo[5.1.0]oct-1(7)-en-8-ylidene}pentane-2,4-dione (11): Compound **1** (0.5 g, 4.1 mmol) in dry dichloromethane (8 mL), $Et_3O^+BF_4^-$ in dichloromethane (1 M, 4.3 mL, 4.3 mmol), cupric acetylacetonate (1.1 g, 4.1 mmol). After purification of the crude product by heating to reflux in diethyl ether, yield 0.3 g of **11** (36%), light yellowish crystals, m.p. 127−130 °C with decomposition. − IR (KBr): ṽ = 2948 cm^{-1} (CH), 1861 (C=C), 1629 (C=O), 1480 (CH). − UV/Vis (methanol): λ_{max} (lg ε) = 274 (4.8), 250 (4.2). ^1H NMR ($CDCl_3$): δ = 1.78−1.85 (m, 2 H, CH_2), 1.98−2.05 (m, 4 H, CH_2), 2.41 (s, 6 H, CH_3), 2.94−2.98 [t, *J* = 6.2 Hz, 4 H, CH_2]. − ^{13}C NMR ($CDCl_3$): 27.3, 27.3, 30.0 (5 C, CH_2), 29.7 (2 C, CH_3), 103.0, 148.4, 157.7 (4 C, quaternary C), 195.6 (2 C, C=O). − MS (EI, 70 eV); *m/z* (%): 204 (35) [M^+], 189 (80) [M^+ − CH_3], 147 (71) [M^+ − CH_3 − CH_3CO], 43 (100) [CH_3CO]. − $C_{13}H_{16}O_2$ (204.3): calcd. C 76.44, H 7.89; found C 76.46, H 7.88.

2-{Bicyclo[5.1.0]oct-1(7)-en-8-ylidene}-1-phenylbutane-1,3-dione (12): Compound **1** (0.50 g, 4.1 mmol) in dry dichloromethane (8 mL), $Et_3O^+BF_4^-$in dichloromethane (1 M, 4.3 mL, 4.3 mmol), cupric benzoylacetonate (1.58 g, 4.1 mmol). Chromatographic separation and addition of diethyl ether to the resulting yellow oil gave 0.27 g of **12** (25%), as light yellow crystals, m.p. 97−98 °C. − IR (KBr): ṽ = 2937 cm^{-1} (CH), 1865 (C=C), 1617 (C=O), 1474, 1352

(CH), 1328. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 246 nm (4.3), 274 (4.2). − ^{1}H NMR ($CDCl_3$): δ = 1.69−1.96 (m, 8 H, CH_2), 2.59 (s, 3 H, CH_3), 2.97−3.01 [t, J = 6.3 Hz, 2 H, CH_2], 7.38−7.50 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 25.8, 27.2, 27.7, 29.7, 29.9 (5 C, CH_2), 30.1 (CH_3), 128.0, 128.2, 130.0 (5 C, aromatic C), 102.3, 142.8, 149.9, 156.2, 159.3 (5 C, quaternary C), 194.4, 197.2 (C=O). − MS (EI, 70 eV); m/z (%): 266 (38) [M^+], 251 (60) [$M^+ - CH_3$], 105 (100) [$C_8H_9^+$]. − $C_{18}H_{18}0_2$ (266.1): calcd. C 81.18, H 6.81; found C 80.89, H 6.80.

2-{Bicyclo[5.1.0]oct-1(7)-en-8-ylidene}-3-oxobutaneacetanilide (13): Compound **1** (0.50 g, 4.1 mmol) in dry dichloromethane (8 mL), $Et_3O^+BF_4^-$ in dichloromethane (1 M, 4.3 mL, 4.3 mmol), cupric 3-oxobutaneacetanilide (1.69 g, 4.1 mmol). Heating the dark oil to reflux in diethyl ether gave 0.50 g of **13** (44%), as white crystals, m.p. 244−245 °C. − IR (KBr): $\tilde{\nu}$ = 3118 cm^{-1} (NH), 2936 (CH), 1869 (C=C), 1654, 1589, 1537 (C=O, C=O−NH), 1482 (CH). − UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 274 nm (4.7). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72−1.98 (m, 6 H, CH_2), 2.79−2.85 [t, J = 6.2 Hz, 2 H, CH_2], 3.00−3.07 [t, J = 6.0 Hz, 2 H, CH_2], 6.94−6.95 (m, 1 H, aromatic H), 7.18−7.26 (m, 2 H, aromatic H), 7.55−7.60 (m, 2 H, aromatic H), 11.41 (s, 1 H, NH). − ^{13}C NMR ($CDCl_3$): δ = 26.6, 27.0, 27.6, 29.7, 29.8 (5 C, CH_2), 27.8 (CH_3), 120.0, 122.7, 128.5 (5 C, aromatic C), 94.5, 139.2, 148.5, 154.3, 160.1 (5 C, quaternary C), 165.0 (C=O−NH), 195.5 (C=O). MS (EI, 70 eV); m/z (%): 281 (17) [M^+], 189 (100) [M^+ − NH, − C_6H_5]. − $C_{18}H_{19}NO_2$ (281.1): calcd. C 76.83, H 6.81, N 4.98; found C 76.72, H 6.77, N 4.98.

3-Hydroxy-4,4,7,7-tetramethyl-3-(3,3,6,6-tetramethylcyclohex-1-enyl)-4,5,6,7-tetrahydro-3*H*-isobenzofuran-1-one (16): $LiAlH_4$ (0.07 g, 1.8 mmol) was suspended in dry diethyl ether (30 mL), and the suspension was cooled to 0 °C. A solution of lactone **15** (0.3 g, 0.9 mmol) and BF_3−diethyl ether (3.4 mL, 27.4 mmol) in dry diethyl ether (30 mL) was added over 15 min. The reaction mixture was stirred for 15 min at 0 °C and then heated to reflux for 2 h. After cooling to room temperature, hydrolysis was carried out with 30 mL aq. NaH_2PO_4 (5%) .The organic layer was washed twice with 20 mL aq. $NaHCO_3$ (5%) and saturated aq. NaCl, and dried with Na_2SO_4. After removal of the solvent under reduced pressure, a yellow oil remained. Column chromatography of the crude product on silica gel (0.32−0.64 Å), with dichloromethane as eluent, gave 0.80 g of **16** (26%), as colorless crystals, m.p. 175−178 °C. − IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (OH), 2928 (CH), 1718 (C=O), 1457 (CH). − UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 244 nm (3.3). − ^{1}H NMR ($CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.21−1.23 (4 × s, 12 H, CH_3), 1.28−1.64 (m, 8 H, CH_2), 3.02 (s, 1 H, OH), 5.87 (s, 1 H, =CH). − MS (HREI, 70 eV); m/z (%): 346.2513 (2.6) [M^+ + H], 313.2142 (12.5) [M^+ − CH_3, − H_2O], 165.1239 (100) [M^+ − $C_{11}H_{17}O_2$]. − $C_{22}H_{33}O_3$ (345.2): calcd. C 76.25, H 9.89; found C 75.88, H 10.01.

X-Ray Diffraction Analysis: Data collection was carried out with an Enraf−Nonius CAD4 diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 nm) and an ω/2Θ scan. Structure solution and refinement were performed with the program MolEN[35], see Tables 5 and Table 6.

Table 5. Experimental details of the X-ray diffraction analysis and refinement

Compound	**1**	**3a**	**4b**	**5a**	**7a**
Formula	$C_8H_{10}O$	$C_{14}H_{15}N_2O_2BF_4$	$C_{14}H_{16}NClO_4$	$C_{20}H_{20}NBF_4$	$C_{23}H_{26}NBF_4$
Molecular mass	122.2	330.1	297.7	361.2	403.3
Crystal grown by/from	sublimation	CH_3OH	C_2H_5OH/CH_3CN	CH_3OH	$(CH_3)_2CO/(C_2H_5)_2O$
Crystal size [mm]	0.50 × 0.35 × 0.25	0.50 × 0.40 × 0.20	0.45 × 0.40 × 0.15	0.50 × 0.40 × 0.30	0.50 × 0.48 × 0.48
Crystal color	colorless	yellowish	colorless	colorless	colorless
Crystal shape	prisms	needles	prisms	prisms	needles
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	Pn	$P2_1/m$	$P2_1/c$	$P2_1/n$	$Pca2_1$
a [Å]	6.314(1)	10.908(1)	15.925(2)	11.300(2)	13.428(2)
b [Å]	16.683(4)	7.312(1)	6.141(1)	9.197(2)	11.098(2)
c [Å]	6.362(1)	12.083(2)	14.302(1)	17.337(6)	29.391(7)
α [°]	90	90	90	90	90
β [°]	90.55(1)	112.20(1)	91.37(1)	97.27(2)	90
γ [°]	90	90	90	90	90
Volume [Å^3]	670.1(2)	892.3(2)	1398.3(3)	1787(1)	4380(2)
$D_{calcd.}$ [Mg/m^3]	1.21	1.23	1.41	1.34	1.22
Z	4	2	4	4	8
F (000)	264	340	624	752	1696
Temperature [K]	193	193	293	293	193
h_{min}/h_{max}	−8/8	0/14	0/21	0/14	0/17
k_{min}/k_{max}	−22/0	0/9	0/8	0/11	0/14
l_{min}/l_{max}	−8/8	−15/15	−18/18	−22/22	−38/0
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.66	0.66	0.66	0.63	0.66
μ [mm^{-1}]	0.08	0.11	0.29	0.10	0.09
Absorption correction	none	None	numerical	none	None
Refl. collected	3239	1861	3477	3871	5366
Refl. unique	1630	1786	3362	3681	5366
Refl. observed	1526	1025	2490	1853	3616
R_{int}	0.019	0.022	0.011	0.021	−
Variables	243	169	206	315	639
Solution method	SHELXS-86[37]	SHELXS-86[37]	SHELXS-86[37]	MULTAN[38]	SHELXS-86[37]
$(\Delta/\sigma)_{max}$	< 0.001	0.03	0.002	< 0.01	< 0.01
R	0.036	0.095	0.048	0.046	0.043
R_W	0.092	0.281	0.142	0.053	0.104
S (Gof)	1.05	1.26	1.19	2.05	1.06
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.31	0.51	0.31	0.28	0.20
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.12	−0.43	−0.27	−0.09	−0.18

Table 6. Experimental details of the X-ray diffraction analysis and refinement

Compound	**10**	**11**	**13**	**14**	**15**	**16**
Formula	$CuC_{26}H_{32}O_4B_2F_8 \cdot 2\ CH_3OH$	$C_{13}H_{16}O_2$	$C_{18}H_{19}O_2N$	$C_{16}H_{20}O_2$	$C_{22}H_{32}O_2$	$C_{22}H_{34}O_3$
Molecular mass	709.8	204.3	281.3	244.3	328.5	346.5
Crystal grown by/from	CH_3OH	C_6H_6/petroleum ether	$(C_2H_5)_2O/CH_2Cl_2$	$CH_2Cl_2/n\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$
Crystal size [mm]	0.45 × 0.45 × 0.10	0.50 × 0.50 × 0.50	0.50 × 0.45 × 0.45	0.5 × 0.45 × 0.42	0.50 × 0.40 × 0.35	0.30 × 0.30 × 0.20
Crystal color	light blue	colorless	colorless	colorless	colorless	colorless
Crystal shape	rhombic	prisms	irregular	prisms	prisms	needles
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	18.132(3)	17.395(3)	9.463(1)	8.975(1)	8.233(2)	8.787(2)
b [Å]	7.145(1)	7.784(1)	9.475(1)	14.947(3)	11.823(2)	12.329(3)
c [Å]	12.754(2)	17.032(2)	8.929(1)	9.865(1)	20.167(4)	18.789(3)
α [°]	90	90	110.39(1)	90	90	90
β [°]	104.17(1)	101.01(1)	96.90(1)	93.74(1)	90	90
γ [°]	90	90	84.65(1)	90	90	90
Volume [$Å^3$]	1602.0(4)	2264(1)	743.8(2)	1320.6(6)	1963(1)	2035.5(8)
$D_{calcd.}$ [Mg/m^3]	1.47	1.20	1.26	1.23	1.11	1.13
Z	2	8	2	4	4	4
F (000)	734	880	300	528	720	760
Temperature [K]	223	293	293	293	293	293
h_{min}/h_{max}	0/23	0/22	−12/12	0/11	0/10	0/11
k_{min}/k_{max}	0/8	0/10	0/12	0/19	0/15	0/16
l_{min}/l_{max}	−16/16	−22/22	−11/11	−13/13	0/26	0/24
$(\sin \theta/\lambda)_{max}$ [$Å^{-1}$]	0.66	0.66	0.66	0.66	0.63	0.66
μ [mm^{-1}]	0.77	0.074	0.08	0.074	0.64	0.07
Absorption correction	Psi-Scan	none	none	none	none	none
Refl. collected	3858	2808	3794	3340	2666	2815
Refl. unique	3747	2722	3578	3150	2666	2365
Refl. observed	3068	1815	2574	2082	1828	1874
R_{int}	0.012	0.017	0.010	0.012	−	0.041
Variables	290	200	219	243	274	267
Solution method	SHELXS-86[37]	MULTAN[38]	SHELXS-86[37]	MULTAN[38]	MULTAN[38]	SHELXS-86[37]
$(\Delta/\sigma)_{max}$	0.03	<0.01	0.002	<0.01	0.02	<0.001
R	0.035	0.043	0.076	0.043	0.059	0.055
R_W	0.096	0.053	0.231	0.050	0.069	0.131
S (Gof)	1.21	2.21	1.23	2.08	2.99	1.12
$(\Delta\rho)_{max}$ [e $Å^{-3}$]	0.35	0.18	0.30	0.14	0.26	0.17
$(\Delta\rho)_{min}$ [e $Å^{-3}$]	−0.42	−0.15	−0.44	−0.22	−0.11	−0.19

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