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# Competition Between Cheletropic and Homocheletropic Additions of Sulfur Dioxide to 2,3,5,6-Tetrakis(methylene)bicyclo[2.2.n]alkanes. Crystal and Molecular Structures of two 3-Thiabicyclo[3.1.0]hexane 3,3-Dioxide Derivatives.

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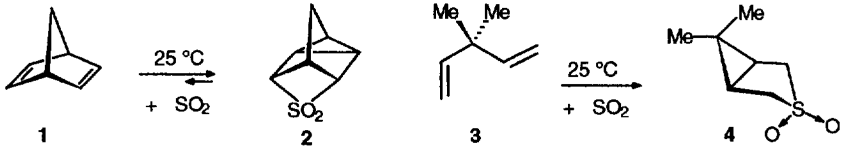
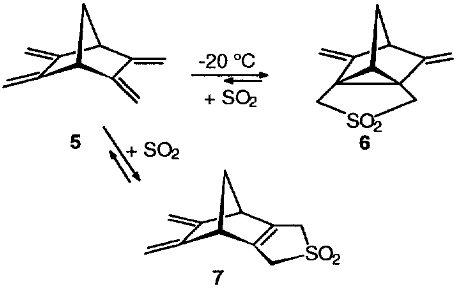
***Abstract.*** *At -20°C, $SO_2$ undergoes homocheletropic addition with 7,7-dimethyl[2.2.1]hericene (**18**) to give (1R,5S)-6,10-dimethylidene-8-isopropylidene-3-thiatetracyclo[5.2.1.$0^{1,5}$.$0^{5,9}$]decane 3,3-dioxide (**21**). This sulfolane is isomerized into (1R,7S)-8,9-dimethylidene-10-isopropylidene-4-thiatricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene 4,4-dioxide (**22**). At 20°C, the equilibrium ratio [**21**]/[**22**] = 4:1, the sulfolane being slightly more stable than the isomeric sulfolene, in contrast with the reactions of $SO_2$ with 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane and 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene. While 2,3,5,6,7-pentamethylidenebicyclo[2.2.2]octane (**19**) and [2.2.2]hericene (**20**) react with $SO_2$ to give first the corresponding monosulfolenes (1SR,7RS)-8,9,10-trimethylidene-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-2(6)-ene 4,4-dioxide (**24**) and 8,9,10,11-tetramethylidene-4-thiatricyclo[5.2.2.$0^{2,6}$]undec-2(6)-ene 4,4-dioxide (**27**) respectively, these adducts undergo homocheletropic additions concurrently with the cheletropic additions of $SO_2$ under conditions of kinetic control, giving (1SR,2SR,8RS,10SR)-9-methylidene-5,12-dithiapentacyclo[6.5.1.$0^{1,10}$.$0^{2,10}$,$0^{3,7}$]tetradec-3(7)-ene 5,5,12,12-tetraoxide (**25**) and (1R,10S)-9,14-dimethylidene-5,12-dithiapentacyclo[6.5.1.$0^{1,10}$.$0^{2,10}$.$0^{3,7}$]tetradec-3(7)-ene 5,5,12,12-tetraoxide (**28**), respectively. At 20°C **25** was partly isomerized into the bissulfolene 13-methylidene-4,10-dithiatetracyclo[5.5.2.$0^{2,6}$.$0^{8,12}$]tetradeca-2(6),8(12)-diene 4,4,10,10-tetraoxide (**26**) ([**25**]/[**26**] = 2:1), whereas **28** was completely converted to the more stable bissulfolene 13,14-dimethylidene-4,10-dithiatetracyclo-[5.5.2.$0^{2,6}$.$0^{8,12}$]tetradeca-2(6),8(12)-diene 4,4,10,10-tetraoxide (**29**). Single crystal X-ray diffraction studies on 6,6-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**4**) and 6,11-dimethylidene-3-thiatetracyclo-[5.3.1.$0^{1,5}$.$0^{5,10}$]undec-8-ene 3,3-dioxide (**12**) revealed unusual bond elongations for the $\sigma$ bond connecting C(1) and C(5) in 3-thiabicyclo[3.1.0]hexane 3,3-dioxide systems.*

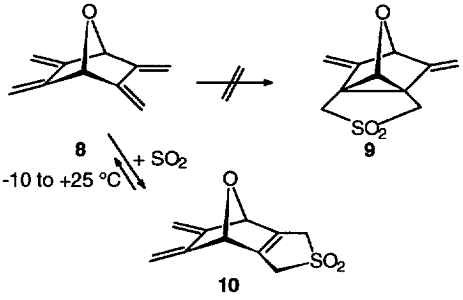
**Introduction.** - Homoconjugated dienes can be rearranged into conjugated 1,3-dienes in the presence of $SO_2$ *via* ene reactions.[1] In the cases of norbornadiene (**1**) and 3,3-dimethylpenta-1,4-diene (**3**) that cannot undergo ene reactions, their reactions with $SO_2$ give the corresponding sulfolanes **2**[2] and **4**,[3] respectively, resulting from homocheletropic additions in a $[_{\omega}2_s+_{\pi}2_s+_{\pi}2_s]$ fashion.[4] When 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**5**)[5] is allowed to react at -20°C with an excess of $SO_2$, the sulfolane **6** is formed as single product. At 0°C, **6** undergoes slow cycloreversion into **5** + $SO_2$ and then formation of the more stable sulfolene **7** resulting from



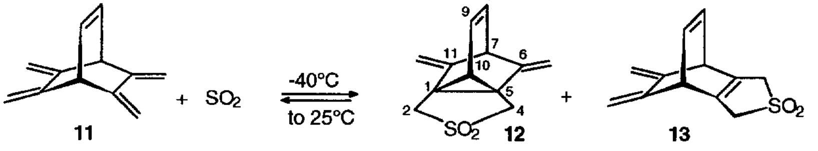
**1** **2** **3** **4**

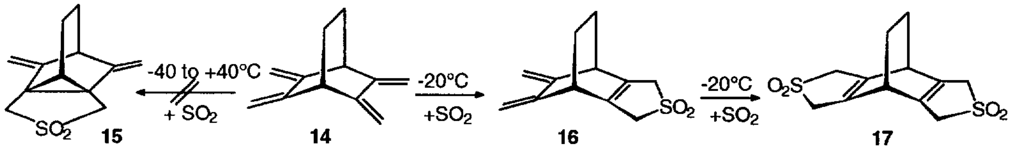
the cheletropic [$_{\omega}2_s+_{\pi}4_s$] addition of an exocyclic 1,3-diene unit. At 25°C, an equilibrium constant K = [**7**]/[**6**] ≅ 5:1 is observed by $^1$H-NMR ($CD_2Cl_2/SO_2$ in excess). In this case, the homocheletropic addition **5** + $SO_2$ → **6** is kinetically favoured but thermodynamically disfavoured compared with the cheletropic addition **6** + $SO_2$ → **7**.[3]

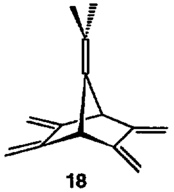


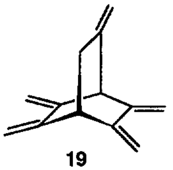


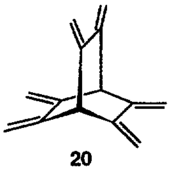
In contrast, 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**8**)[6] does not undergo the homocheletropic addition of $SO_2$ between -30 and +30°C. Above -10°C, slow formation of sulfolene **10** is observed.[3] Between -40°C and 25°C, 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**11**) reacts with $SO_2$ to give a 1:1 mixture of sulfolane **12** and sulfolene **13**. Above 25°C, **12** is isomerized into **13**. In contrast to **11**, 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**14**) gives none of the expected sulfolane **15** between -40 and +40°C. Instead the sulfolene **16** is formed, which adds a second equivalent of $SO_2$ to give the bis-sulfolene **17**. Tetraenes **5**, **8** and pentaene **11** never produced the corresponding bis-sulfolenes when allowed to react with a large excess of $SO_2$ due to the increase in strain between the monosulfolenes and bissulfolenes.[3,7] In order to establish the possible factors intervening in the kinetic competition between cheletropic and homocheletropic additions of $SO_2$ to exocyclic polyenes grafted onto bicyclic skeletons, we have studied the reactions of $SO_2$ with 7,7-dimethyl-





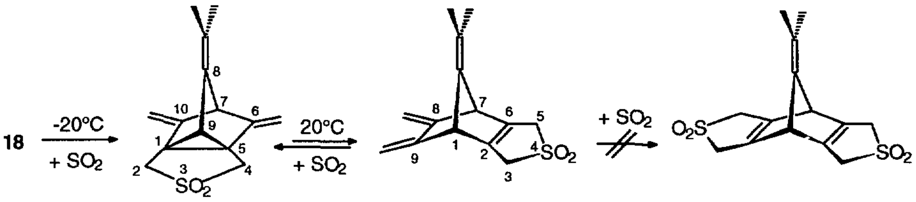

**18**


**19**


**20**

[2.2.1]hericene (**18**),[8] 2,3,5,6,7-pentamethylidenebicyclo[2.2.2]octane (**19**)[9] and [2.2.2]hericene (**20**).[10] The results suggest that the competition depends on subtle geometry differences including the distance between the methylidene units of the 1,3-diene and 1,4-diene moieties. When the bicyclic skeleton contains a heteroelement, a differential inductive effect might also play a role on the kinetic competition between the cheletropic and homocheletropic addition. We also report the single crystal molecular structures of the bicyclic and tetracyclic sulfolanes **4** and **12**, respectively.

**Results.** - Because of the striking reactivity difference between tetraenes **5** and **8**, it was necessary to look at the reactions of $SO_2$ with another 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane system. With its isopropylidene group at C(7), **18** was expected to imitate both tetraene **5** and **8** in terms of geometry factors and to be situated in-between these two systems in terms of the inductive effects introduced by the C(7) or O(7) bridge. At -20°C, **18** added $SO_2$ to give selectively the corresponding sulfolane **21** which at 20°C underwent homocheletropic elimination giving **18** + $SO_2$ which equilibrated with the sulfolene **22**. An equilibrium constant K = [**22**]/[**21**] = 1:4 was measured at this temperature, suggesting that the sulfolane, in this case, is slightly more stable than the isomeric sulfolene, which is contrary to what was observed for the pairs **6**/**7** and **12**/**13**. At higher temperature and in concentrated $SO_2$, no product of double addition of $SO_2$ with **18** could be detected. This is consistent with the fact that the bicyclo[2.2.1]hepta-2,5-diene system **23** is more strained than **22**.[7, 11] The greater thermodynamic stability of the tetracyclic sulfolane **21** compared with that of the tricyclic sulfolene **22** is not readily explained (see below).

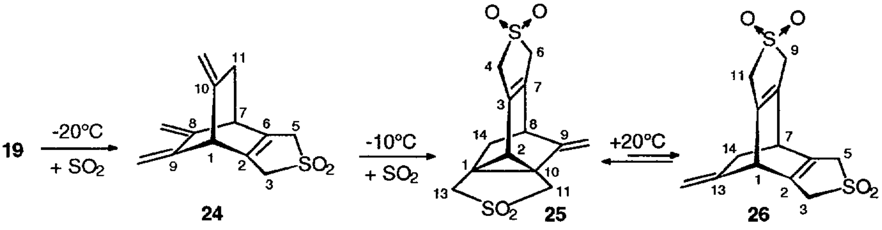


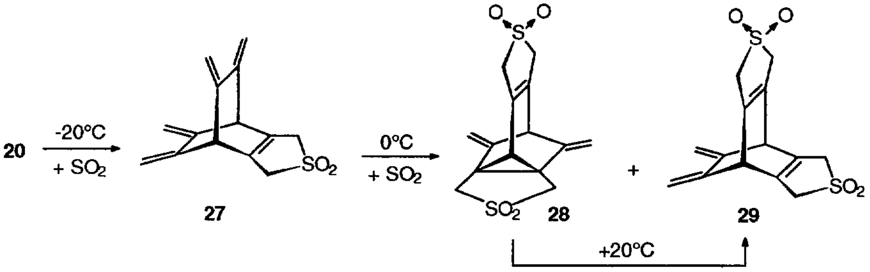
**21** **22** **23**

Because of the dramatic difference in reactivity of $SO_2$ toward pentaene **11** and tetraene **14** under conditions of kinetic control, it was felt that the reactions of $SO_2$ with the exocyclic pentaene **19** and hexaene **20**, all bicyclo[2.2.2]octane systems, would give an insight into the competition between homocheletropic and cheletropic additions.

In the presence of 1-10 equivalents of $SO_2$ in $CD_2Cl_2$, pentaene **19** added one equivalent of $SO_2$ and generated the corresponding sulfolene **24** .The same compound was formed at -20°C or at +25°C. Therefore, pentaene **19** imitates tetraene **14** in terms of its reactivity toward $SO_2$; no trace of any product of homocheletropic addition of $SO_2$ could be detected. Interestingly, in the presence of a large excess of $SO_2$, the bis-adduct **25** was formed nearly quantitatively after 24 h at -10°C. Due to the endocyclic double bond of the monoadduct **24**, the exocyclic triene moiety of this compound behaves as the exocyclic tetraene moiety of pentaene **11** causing the homocheletropic addition of $SO_2$ to be preferred to the cheletropic addition. At 20°C, **25** was partly isomerized into the bissulfolene **26** ([**25**]/[**26**] = 2:1). At -20°C [2.2.2]hericene (**20**) had a reactivity pattern toward $SO_2$ similar to that of exocyclic pentaene **19**. Indeed, **20** reacted with an excess of

$SO_2$ giving sulfolene **27**. At 0-20°C the latter added a second equivalent of $SO_2$ giving a 55:45 mixture of **28** and **29**. After prolonged standing at 20°C **28** was completely isomerized into **29**. These results demonstrate again that exocyclic tetraenes grafted onto bicyclo[2.2.2]octane can undergo the homocheletropic addition of $SO_2$ only if the bicyclic system possesses an endocyclic double bond, which is the case with **11**, **24** and **27** and not with **14**, **19** and **20**. The lower relative stability of **28** compared with that of **25** arises probably from the presence of one more trigonal carbon center in the bicyclic skeleton of the former than in the latter sulfolane.

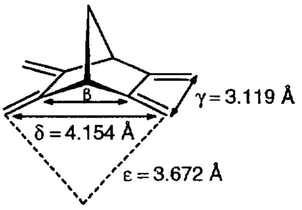




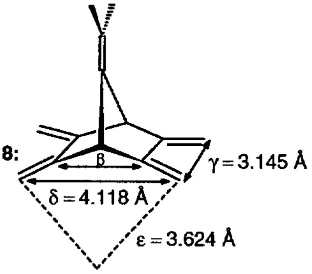
The results reported here demonstrate that subtle changes in the bicyclic skeleton of the monocyclic polyenes can have a significant effect on the competition between the homocheletropic and cheletropic additions of $SO_2$. For both type of reactions, the rate constants varied in a relatively narrow range.

**Discussion.** - In order to hazard an explanation for the observed results we calculated the optimized geometries of polyenes **5**, **8**, **11**, **14**, **18**, **19**, **20**, **24** and **27** (see Table 1) using three different semi-empirical calculation methods. The AM1 routine gave for [2.2.2]hericene (**20**) geometry parameters that were the closest to those obtained experimentally for the crystalline state.[10b]

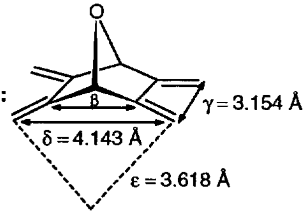
**5:**



**18:**



**8:**



The *Diels-Alder* reactivity depends on the 1,4-distance separating centers C(1) and C(4) of a 1,3-diene moiety.[12] As expected, the calculated geometry parameters show very small differences within each of the bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane series, however differences are significantly larger between these two series. The 1,4-distance ($\gamma$) between the conjugated exocyclic diene units of the bicyclo[2.2.1]heptane systems are nearly the same (3.119 Å - 3.154 Å). The 1,5-distance ($\delta$) separating the terminal centers of the homoconjugated moieties as well the distance ($\varepsilon$) separating these centers from the intersection of the perpendiculars to the 1,3-diene units taken at these centers are smaller in the 7,7-dimethyl[2.2.1]hericene (**18**) than in tetraene **5**. This could explain the greater relative stability of sulfolane **21** compared with that of **6** ([**21**]/[**22**] ≅ 4:1 and [**6**]/[**7**] ≅ 1:5 at 20-25°C, under equilibrium conditions).

Table 1. Calculated geometries of exocyclic polyenes for completely optimized structures

| Polyene | Distance $\beta$ | $\gamma$ | $\delta$ | $\varepsilon$ (in Å) |
|---|---|---|---|---|
| **5** | **2.4256**[a)] | **3.1192** | **4.1537** | **3.6720** |
| | *2.4186*[b)] | *3.1168* | *4.1479* | |
| | (2.4101)[c)] | (3.0224) | (4.1401) | |
| **18** | **2.4313** | **3.1447** | **4.1179** | **3.6236** |
| | *2.4219* | *3.1392* | *4.1166* | |
| | (2.4164) | (3.0113) | (4.1485) | |
| **8** | **2.4425** | **3.1538** | **4.1431** | **3.6177** |
| | *2.4367* | *3.1469* | *4.1409* | |
| | (2.4306) | (3.0171) | (4.1681) | |
| **14** | **2.4429** | **3.0211** | **4.3284** | **4.3675** |
| | *2.4372* | *3.0101* | *4.3290* | |
| | (2.4271) | (2.9299) | (4.3172) | |
| **19** | **2.4372-2.4391** | **3.0215** | **4.3111-4.3532** | **4.3496** |
| | *2.4329-2.4405* | *3.0099* | *4.3194-4.3560* | |
| | (2.4237-2.4304) | (2.9314) | (4.3070-4.3217) | |
| **20** | **2.4402** | **3.0276** | **4.3222** | **4.3348** |
| | *2.4365* | *3.0109* | *4.3207* | |
| | (2.4267) | (2.9352) | (4.3050) | |
| **11** | **2.4323** | **3.0271** | **4.2947** | **4.2036** |
| | *2.4288* | *3.0208* | *4.2932* | |
| | (2.4181) | (2.9351) | (4.2884) | |
| **24** | **2.4279** | **3.0292** | **4.3025** | **4.2252** |
| | *2.4255* | *3.0238* | *4.3026* | |
| | (2.4127) | (2.9284) | (4.3030) | |
| **27** | **2.4316** | **3.0277** | **4.2872** | **4.1969** |
| | *2.4372* | *3.0177* | *4.2969* | |
| | (2.4122) | (2.9346) | (4.2838) | |

a) AM1 method[13]

b) PM3 method[14]

c) MM+ method[15]

The geometry parameter ε calculated for the ether analogue **8** is smaller than that of **5** and **18**. It does not explain the non-observation of homocheletropic addition of $SO_2$ to **8**. Although at this stage it is clear that the oxa bridge in **8** plays a specific role which is probably associated with its inductive effect, it is not obvious why there should be a differential inductive effect for the homocheletropic and cheletropic additions of these exocyclic tetraenes.

In the bicyclo[2.2.2]octane series (**14**, **19**, **20**, **11**, **24**, **27**) the distances β, γ are nearly the same whatever the nature of the bridge. The most sensitive geometry parameter is the distance ε. In the case of **14**, **19** and **20** which are bicyclo[2.2.2]octane systems (ethano bridge), the distance ε is ca. 0.15 Å larger than in the case of **11**, **24** and **27** which are bicyclo[2.2.2]oct-2-ene derivatives (ethyleno bridge). While the former systems do not undergo the homocheletropic addition concurrently with the cheletropic addition of $SO_2$, the latter do generate the corresponding sulfolanes **12**, **25** and **28**, respectively, under conditions of kinetic control. It must be noted here that the gas phase ionisation potentials of 2,3-dimethylidenebicyclo[2.2.2]octane, 5,6-dimethylidene-bicyclo[2.2.2]oct-7-ene,[16] **14**, **19**, **20** and **21**[17] are nearly the same,[7] which suggests that a hypothetical homoconjugative interaction between the endocyclic double bond and the exocyclic diene moieties in **11**, **24** and **27** is not an important factor and that it cannot be held responsible for the relatively facile homocheletropic additions of $SO_2$ to these exocyclic polyenes. At this stage we can propose that the geometries of the 5,6,7,8--tetramethylidenebicyclo[2.2.2]oct-2-enes are better suited than those of 2,3,5,6-tetramethylidenebicyclo-[2.2.2]octanes to the competitive homocheletropic addition of $SO_2$.

**Crystalline Molecular Structures.** - The structures of the new sulfolanes **21**, **25** and **28**, and of the new sulfolenes **22**, **26** and **29** were given by their $^1H$ and $^{13}C$-NMR (see Experim. Part). Since the literature does not report the crystalline molecular structure of any 3-thiabicyclo[3.1.0]hexane 3,3-dioxide derivatives, we have obtained single crystals of sulfolanes **4** and **12** and have submitted them to X-ray diffraction studies. Selected data are given in Tables 2 and 3 and the ORTEP[18] representations of **4** and **12** are given in Fig. 1 and 2, respectively. Complete X-ray diffraction analyses are deposited in the Cambridge Crystallographic Data File.

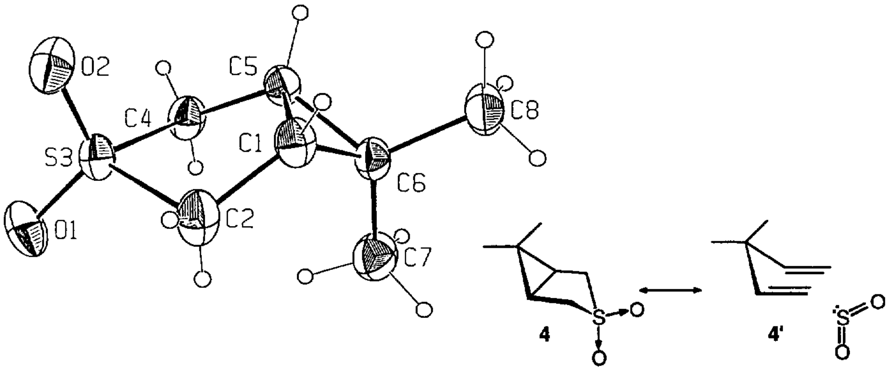


Figure 1. ORTEP representation of sulfolane **4** (50% probability, for heavy atoms).

Table 2. Selected bond distances (Å), bond angles and torsion angles (°) of **4**.[a)]

| bond lengths | | | bond angles | | |
|---|---|---|---|---|---|
| C(1)-C(5) | 1.533 (8) | 1.522 (6)[b)] | C(1)-C(5)-C(6): | 59.5 (3) | 59.6 (3) |
| C(1)-C(6) | 1.501 (7) | 1.500 (7) | C(5)-C(1)-C(6): | 58.7 (3) | 59.5 (3) |
| C(5)-C(6) | 1.488 (7) | 1.499 (6) | C(2)-S(3)-C(4) | 97.6 (2) | 94.3 (2) |
| C(1)-C(2) | 1.500 (6) | 1.509 (6) | C(1)-C(2)-S(3): | 106.2 (3) | 103.1 (3) |
| C(4)-C(5) | 1.541 (7) | 1.525 (5) | O(1)-S(3)-O(2) | 117.2 (2) | 117.2 (2) |
| C(2)-S(3) | 1.792 (5) | 1.789 (4) | C(7)-C(6)-C(8): | 111.8 (5) | 113.3 (4) |
| C(4)-S(3) | 1.776 (4) | 1.782 (5) | | | |
| S(3)-O(1) | 1.446 (3) | 1.438 (3) | torsional angles | | |
| S(3)-O(2) | 1.436 (4) | 1.442 (4) | C(2)-C(1), C(5)-C(4): | -1.8 (6) | -0.3 (5) |
| C(6)-C(7) | 1.511 (7) | 1.505 (7) | C(2)-C(1), C(5)-C(6): | -113.7 (5) | -115.4 (4) |
| C(6)-C(8) | 1.487 (6) | 1.510 (6) | C(1)-C(2), S(3)-C(4): | 21.9 (4) | 36.8 (4) |

a) There are three independent molecules in the asymmetric unit, one of which being disordered. The data for the two ordered molecules are given here.

b) Standard deviations

Chair-like conformations are found for the 3-thiabicyclo[3.1.0]hexane 3,3-dioxide moieties of **4** and **12**. The X-ray data collected for **4** (3 independent molecules in the asymmetric unit) suggest that the puckering of the sulfolane five-membered ring can vary within large limits (see Table 2, torsional angle C(2)-C(1), S(3)-C(4)). This can be attributed to the intrinsic flexibility of the five-membered ring. Noteworthy is the observation that the σC(1),C(5) bond in **4** is longer than the σC(1),C(6) and σC(5),C(6) bonds. A similar observation is made with **12** which shows longer σC(1),C(5) bond than σC(1),C(10) and σC(5),C(10) bonds. In **4** the bond length differentiation of the cyclopropane unit varies between 0.20 and 0.45 Å. In **12** it reaches the average value of 0.42 Å. By inspection of X-ray diffraction data reported for other bicyclic systems incorporating a cyclopropane unit, bond elongation of the σ bond connecting the two bridgehead centers has not been seen thus far. Examples of such structures are given in Table 4.

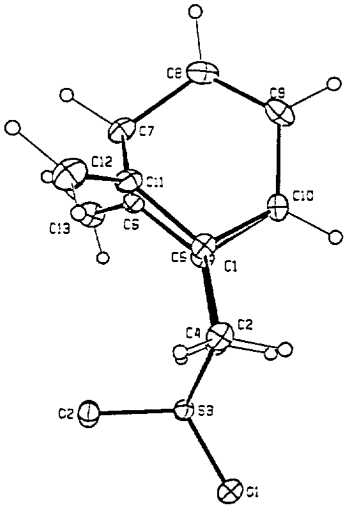


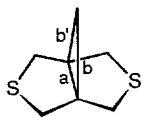
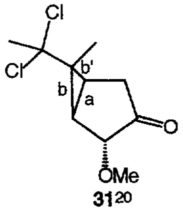
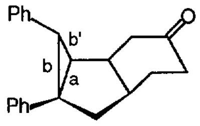
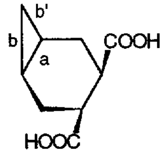
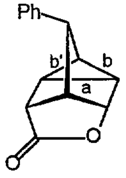
Figure 2: ORTEP representation of **12** (50% probability for heavy atoms)

The C(1)-C(5) bond elongation noted for **4** and **12** can be interpreted in terms of structures in the ground state that approach those of the transition state of the homocheletropic elimination of $SO_2$, as indicated with the limiting structures **4** ↔ **4'**. This is possible because of the relatively low enthalpy barrier for this reaction, a feature that does not exist with systems **30-32** which, in principle, could undergo cheletropic eliminations of sulfur, carbon monoxide and carbene, respectively, all being processes requiring much higher activation energies. Derivatives **33** and **34** can, in principle, undergo retro-homo-Diels-Alder reactions[24] with the formation of fumaric acid and carbon dioxide, respectively. These two reactions also require much higher activation energies than the homocheletropic elimination of $SO_2$ in **4** and **12** and thus structures **33** and **34**, do not show in their ground state, the same bond length differentiation for their cyclopropane moieties as for **4** and **12**.

Table 3. Selected bond distances (Å), bond angles and torsion angles (°) of **12**.

| bonds lengths | | bond angles | |
|---|---|---|---|
| C(1)-C(5) | 1.569 (3) | C(1)-C(10)-C(5) | 61.8 (2) |
| C(1)-C(10) | 1.525 (4) | C(1)-C(5)-C(10) | 59.0 (2) |
| C(5)-C(10) | 1.528 (4) | C(2)-S(3)-C(4) | 96.6 (1) |
| C(1)-C(2) | 1.501 (4) | C(1)-C(2)-S(3) | 103.3 (2) |
| C(5)-C(4) | 1.497 (3) | O(1)-S(3)-O(2) | 116.9 (1) |
| C(2)-S(3) | 1.804 (3) | C(9)-C(10)-H(8) | 118 (1) |
| C(4)-S(3) | 1.804 (2) | | |
| S(3)-O(1) | 1.447 (2) | torsional angles | |
| S(3)-O(2) | 1.448 (2) | C(2)-C(1), C(5)-C(4): | -0.2 (3) |
| C(1)-C(11) | 1.485 (3) | C(2)-C(1), C(5)-C(10): | 111.7 (2) |
| C(10)-C(9) | 1.483 (4) | C(1)-C(2), S(3)-C(4): | 32.6 (2) |
| C(8)-C(9) | 1.323 (4) | C(1)-C(5), C(6)-C(13): | -149.8 (3) |
| C(11)-C(12) | 1.324 (4) | C(1)-C(5), C(6)-C(7): | 25.6 (3) |
| C(6)-C(7) | 1.534 (4) | | |
| C(7)-C(8) | 1.512 (4) | | |

Table 4. Summary of single crystal X-ray diffraction data.

| | | | | |
|---|---|---|---|---|
|  |  |  |  |  |
| **30**[19] | **31**[20] | **32**[21] | **33**[22] | **34**[23] |
| a : 1.489<br>b : 1.492<br>b': 1.496 | a : 1.519<br>b : 1.505<br>b': 1.513 | a : 1.507<br>b : 1.514<br>b': 1.525 | a : 1.484<br>b : 1.485<br>b': 1.471 | a : 1.509<br>b : 1.520<br>b': 1.507 |

**Conclusion.** - The reaction of 7,7-dimethyl[2.2.1]hericene (**18**) with $SO_2$ gives first the corresponding sulfolane **21** resulting from a homocheletropic addition. This adduct is formed more rapidly than the corresponding sulfolene **22** resulting from the cheletropic addition of $SO_2$ to a conjugated diene moiety. Sulfolane **21**

is isomerized into sulfolene **22** *via* homocheletropic elimination followed by cheletropic addition of $SO_2$. The sulfolane **21** is slightly more stable than the isomeric sulfolene **22**. This contrasts with the sulfolanes **6** and **12** resulting from the homocheletropic additions of $SO_2$ to 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane (**5**) and 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**11**), respectively, which were found to be less stable than the corresponding sulfolenes **7** and **13** resulting from the cheletropic additions of $SO_2$ to **5** and **11**, respectively. With polyenes grafted on bicyclo[2.2.2]octane skeletons, the homocheletropic additions of $SO_2$ can compete with the cheletropic addition only if the bicyclic system contains an endocyclic double bond (bicyclo[2.2.2]oct-2-ene derivatives). While 2,3,5,6,7-pentamethylidenebicyclo[2.2.2]octane (**19**) and [2.2.2]hericene (**20**) reacted with $SO_2$ to give first the corresponding monosulfolenes **24** and **27**, respectively, these adducts underwent homocheletropic additions concurrently with the cheletropic additions of $SO_2$ under conditions of kinetic control giving the sulfolanes **25** and **28**. They are unstable at 20°C and underwent homocheletropic eliminations of $SO_2$. This work demonstrates that very subtle changes in the geometry of the exocyclic polyenes can affect the competition between the homocheletropic and cheletropic addition of $SO_2$. Single crystal X-ray diffraction studies disclosed unusual bond elongation for the $\sigma$ bond connecting C(1) and C(5) in 3-thiabicyclo[3.1.0]hexane 3,3-dioxide moieties of 6,6-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide (**4**) and (1*R*,5*S*)-6,11-dimethylidene-3-thiatetracyclo[$5.3.1.0^{1,5}.0^{5,10}$]undec-8-ene 3,3-dioxide (**12**).

## Experimental Part

General. See ref. 25.

*(1*R*,5S)-6,10-Dimethylidene-8-isopropylidene-3-thiatetracyclo[$5.2.1.0^{1,5}.0^{5,9}$]decane 3,3-Dioxide* (**21**). In a pyrex tube a solution of **18**[8] (48 mg, 0.26 mmol) in anh. $CD_2Cl_2$ (0.3 ml) was degassed on the vac. line by freeze/thaw cycles. $SO_2$ (0.81g, 12.7 mmol) purified by flowing through a column of alkaline alumina was condensed at -196°C. The pyrex tube was sealed *in vacuo* and allowed to stand at -20°C for 24 h. After freezing in liq. $N_2$, the tube was opened, the solid was allowed to melt, and the liquid poured into a flask cooled to -15°C. The solvent and $SO_2$ was evaporated *in vacuo*, giving 62 mg (96%), colourless solid, m.p. 98-99°C (dec.), which decomposed at 20°C on standing. IR (KBr): 3070, 2990, 2980, 2920, 2850, 1730, 1665, 1440, 1410, 1370, 1290, 1230, 1215, 1140, 1100, 880, 870, 840, 810. $^1$H-NMR (400 MHz, $CD_2Cl_2/SO_2$, -20°C): 4.96, 4.76 (2s, $H_2C{=}C(6)$, $H_2C{=}C(10)$); 3.80 (d, $^2J = 14.0$ Hz, Heq-C(2), Heq-C(4)); 3.49 (s, H-C(7)); 3.18 (d, $^2J = 14.0$ Hz, Hax-C(2), Hax-C(4)); 2.83 (br. s, H-C(9)); 1.69 (s, $Me_2C{=}C(8)$). $^{13}$C-NMR (100.61 MHz, $CD_2Cl_2/SO_2$, -20°C): 150.4 (s, C(6), C(10)); 134.4 (s, C(8)); 120.8 (s, $Me_2\mathit{C}{=}C(8)$); 99.9 (t, $^1J$(C,H) = 160 Hz, $H_2\mathit{C}{=}C(6)$, $H_2\mathit{C}{=}C(10)$); 50.7 (t, $^1J$(C,H) = 144 Hz, C(2), C(4)); 48.5 (d, $^1J$(C,H) = 158 Hz, C(7)); 39.1 (d, $^1J$(C,H) = 179 Hz, C(9)); 38.8 (s, C(1), C(5)); 20.2, 19.4 (2q, $^1J$(C,H) = 126 Hz, $\mathit{Me}_2C{=}C(8)$). CI-MS 248 ($M^{+\bullet}$, 2), 185 (20), 184 (23), 170 (17), 169 (100), 154 (18), 153 (14), 141 (20), 129 (15), 128 (23), 117 (17), 115 (35), 91 (33), 77 (14).

*Data for (1*R*,7S)-8,9-Dimethylidene-10-isopropylidene-4-thiatricyclo[$5.2.1.0^{2,6}$]dec-2(6)-ene 4,4-Dioxide* (**22**). $^1$H-NMR (360 MHz, $CD_2Cl_2/SO_2$, 40°C): 5.16 (s, 2H, $H_2C{=}C((8Z)$, $H_2C{=}C(9Z)$); 5.00 (s, 2 H, $H_2C{=}C(8E)$, $H_2C{=}C(9E)$); 3.92 (dm, 2 H, $^2J = 16.0$ Hz, H-C(3), H-C(5)); 3.88 (s, 2 H, H-C(1), H-C(7)); 3.71 (dm, 2 H, $^2J = 16.0$ Hz, H'-C(3), H'-C(5)); 1.68 (s, 6 H, 2 $CH_3$). $^{13}$C-NMR (100.61 MHz, $CD_2Cl_2/SO_2$, 23°C): 146.2 (s, C(8), C(9)); 140.8 (s, C(2), C(6)); 139.0 (s, C(10)); 115.5 (s, $\mathit{C}{=}C(10)$); 103.5 (t, $^1J$(C,H) =

159 Hz, $H_2C$=C(8), $H_2C$=C(9)); 56.3 (t, $^1J$(C,H) = 145 Hz, C(3), C(5)); 52.7 (d, $^1J$(C,H) = 148 Hz, C(1), C(7)); 19.7 (q, $^1J$(C,H) = 127 Hz, 2 $CH_3$).

*(1*SR*,7*RS*)-8,9,10-Trimethylidene-4-thiatricyclo[5.2.2.0$^{2,6}$]undec-2(6)-ene 4,4-Dioxide* (**24**). Dry $SO_2$ was bubbled through a solution of **19**$^9$ (104 mg, 0.61 mmol) in anh. $CH_2Cl_2$ (40 ml) at 20°C. After the disappearance of **19** (TLC on silica gel, $CH_2Cl_2$), $N_2$ was bubbled through the solution to remove the excess of sulfur dioxide, and then the solvent was evaporated *in vacuo*. The residue was purified by FC ($CH_2Cl_2$), yielding 102 mg (71%) colourless crystals, m.p. 116°C (dec.). IR (KBr): 3060, 2960, 2900, 1610, 1430, 1400, 1290, 1240, 1145, 1100, 1085, 905, 880, 850. $^1$H-NMR (250 MHz, $CD_2Cl_2$): 5.43, 5.29 (2s, 2 H, $H_2C$=C(9)); 4.99 (dt, 1 H, $^2J$ = 0.9, $^4J$ = 2.4 Hz, H-C=C(10)); 4.96, 4.94 (2s, 2 H, $H_2C$=C(8)); 4.77 (dt, 1 H, $^2J$ = 0.9, $^4J$ = 2.1 Hz, H-C=C(10)); 3.91 (s, 4 H, $H_2C$(3), $H_2C$(5)); 3.76 (s, 1 H, H-C(1)); 3.39 (t, 1 H, $^3J$ = 2.7 Hz, H-C(7)); 2.51 (ddd, 1 H, $^2J$ = 16.3, $^3J$ = 2.7, $^4J$ = 2.1 Hz, H-C(11)); 2.37 (ddd, 1 H, $^2J$ = 16.3, $^3J$ = 2.7, $^4J$ = 2.4 Hz, H'-C(11)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 144.2, 143.6, 142.9 (3s, C(8), C(9), C(10)); 133.7 (s, C(2)); 133.2 (s, C(6)); 107.6 (t, $^1J$(C,H) = 159 Hz, $H_2C$=C(10)); 105.4 (t, $^1J$(C,H) = 158 Hz, $H_2C$=C(8), $H_2C$=C(9)); 57.7 (t, $^1J$(C,H) = 143 Hz, C(3)); 57.4 (t, $^1J$(C,H) = 144 Hz, C(5)); 53.4 (d, $^1J$(C,H) = 141 Hz, C(1)); 43.2 (d, $^1J$(C,H) = 141 Hz, C(7)); 34.3 (t, $^1J$(C,H) = 128 Hz, C(11)). CI-MS ($NH_3$): 252 (M+17, 100), 235 ($M^{+\bullet}$, 1) 188 (18), 171 (37), 170 (18), 155 (11), 141 (3), 128 (3), 115 (4), 91 (3). Anal. calc. for $C_{13}H_{14}O_2S$ (234.31): C 66.65, H 6.03; found: C 66.53, H 5.95.

*(1*SR*,2*SR*,8*RS*,10*SR*)-9-Methylidene-5,12-dithiapentacyclo[6.5.1.0$^{1,10}$.0$^{2,10}$.0$^{3,7}$]tetradeca-3(7)-ene 5,5,12,-12-Tetraoxide* (**25**). In a pyrex tube, a solution of **19**$^9$ (33 mg, 0.19 mmol) in anh. $CD_2Cl_2$ (0.9 ml) was degassed on the vac-line. Dry $SO_2$ (2.57 g, 40 mmol) was added at -196°C. After sealing the tube *in vacuo*, the tube was allowed to stand at -10°C for 24 h. The tube was frozen in liq. $N_2$ and opened. After solvent evaporation, the residue was purified by flash chromatography on a column of silica gel (light petroleum/$Et_2O$ 1:1) giving 43 mg (76%), colourless crystals, m.p. 124-126°C (dec.). IR (KBr): 2990, 2960, 2930, 1665, 1410, 1300, 1240, 1230, 1140, 1130, 1110, 870, 820. $^1$H-NMR (400 MHz, $CDCl_3$): 5.14, 4.86 (2s, $H_2C$=C(13)); 3.83-4.00 (m, $H_2C$(4), $H_2C$(6)); 3.72 (dd, $^2J$ = 13.7, $^5J$ = 1.7 Hz, H-C(11)); 3.64 (dd, $^2J$ = 13.7, $^5J$ = 1.7 Hz, H-C(13)); 3.26 (d, $^2J$ = 13.7 Hz, H'-C(13)); 3.20 (d, $^3J$ = 4.8 Hz, H-C(8)); 3.17 (d, $^2J$ = 13.7 Hz, H'-C(11)); 2.34 (s, H-C(2)); 1.97 (dd, $^2J$ = 11.5, $^3J$ = 4.8 Hz, H-C(14)); 1.58 (d, $^2J$ = 11.5 Hz, H'-C(14)). $^{13}$C-NMR (100.61 MHz, $CDCl_3$): 144.1 (s, C(9)); 130.2 (s, C(7)); 124.3 (s, C(3)); 106.0 (t, $^1J$(C,H) = 160 Hz, $H_2C$=C(9)); 58.3 (t, $^1J$(C,H) = 144 Hz, C(13)); 57.8 (t, $^1J$(C,H) = 144 Hz, C(11)); 56.6 (t, $^1J$(C,H) = 144 Hz, C(6)); 53.2 (t, $^1J$(C,H) = 144 Hz, C(4)); 42.8 (d, $^1J$(C,H) = 145 Hz, C(8)); 34.5 (d, $^1J$(C,H) = 174 Hz, C(2)); 32.8 (s, C(10)); 32.6 (s, C(1)); 32.3 (t, $^1J$(C,H) = 138 Hz, C(14)). CI-MS ($NH_3$): 252, 234 (M-$SO_2$), 187, 170 (M-$SO_2$), 155. Anal. calc. for $C_{13}H_{14}O_4S_2$ (298.37): C 52.33, H 4.73, S 21.49; found: C 52.48, H 4.62, S 21.37.

*Data for 13-Methylidene-4,10-dithiatetracyclo[5.5.2.0$^{2,6}$.0$^{8,12}$]tetradeca-2(6),8(12)-diene 4,4,10,10-Tetraoxide* (**26**). $^1$H-NMR (400 MHz, $CD_2Cl_2/SO_2$, 20°C): 5.05 (t, 1 H, $^4J$= 1.8 Hz, H-C=C(13)); 4.83 (t, 1 H, $^4J$ = 1.6 Hz, H'-C=C(13)); 4.09 (s, 1 H, H(1)); 3.89 (m, 8 H, $H_2C$(3), $H_2C$(5), $H_2C$(9), $H_2C$(11)); 3.79 (t, 1 H, $^3J$ = 2.7 Hz, H-C(7)); 2.31 (ddd, 2 H, $^3J$ = 2.7, $^4J$ = 1.6, $^4J$ = 1.8 Hz, $H_2C$(14)). $^{13}$C-NMR (100.61 MHz, $CD_2Cl_2/SO_2$, 20°C): 143.4 (s, C(13)); 136.2 (s, C(2), C(12)); 135.1 (s, C(6), C(8)); 108.2 (t, $^1J$(C,H) = 159 Hz, $H_2C$=C(13)); 58.1 (t, $^1J$(C,H) = 145 Hz, C(3), C(11)); 57.8 (t, $^1J$(C,H) = 145 Hz, C(5), C(9)); 49.1 (d, $^1J$(C,H) = 146 Hz, C(1)); 39.5 (d, $^1J$(C,H) = 147 Hz, C(7)); 33.3 (t, $^1J$(C,H) = 134 Hz, C(14)).

*(1*R*,10*S*)-9,14-Dimethylidene-5,12-dithiapentacyclo[6.5.1.0$^{1,10}$.0$^{2,10}$.0$^{3,7}$]tetradeca-3(7)-ene 5,5,12,12-Tetraoxide* (**28**). Anh. $SO_2$ (0.66 g, 10.35 mmol) was added to a frozen sol. of **20**$^{10a}$ (14 mg, 0.08 mmol) in anh. $CD_2Cl_2$ (0.39 ml) (NMR tube, vac-line). After sealing the NMR-pyrex tube *in vacuo*, the reaction was

followed at -10°C by 400 MHz $^1$H-NMR. Slow formation of a 55:45 mixture of **28** and **29** was observed. On standing at 20°C, **28** was completely isomerized into **29** in a few hours. $^1$H-NMR (400 MHz, $CD_2Cl_2/SO_2$, 23°C): 5.18, 4.93 (2s, 4 H, $H_2C$=C(9), $H_2C$=C(14)); 3.95 (br. s, 4 H, $H_2C(4)$, $H_2C(6)$), 3.83 (d, 2 H, $^2J$ = 13.5 Hz, Heq-C(11), Heq-C(13)); 3.66 (s, 1 H, H-C(8)); 3.23 (d, 2 H, $^2J$ = 13.5 Hz, Hax-C(11), Hax-C(13)); 2.70 (s, 1 H, H-C(2)). $^{13}$C-NMR (100.61 MHz, $CD_2Cl_2/SO_2$, 23°C): 143.8 (s, C(9), C(14)); 130.3 (s, C(7)); 125.2 (s, C(3)); 105.5 (t, $^1J$(C,H) = 160 Hz, $H_2C$=C(9), $H_2C$=C(14)); 57.9 (t, $^1J$(C,H) = 145 Hz, C(4), C(6)); 53.6 (t, $^1J$(C,H) = 144 Hz, C(11), C(13)); 50.3 (d, $^1J$(C,H) = 148 Hz, C(8)); 39.0 (d, $^1J$(C,H) = 170 Hz, C(2)); 37.6 (s, C(1), C(10)).

Single Crystal X-ray diffraction of *6,6-dimethyl-3-thiabicyclo[3.1.0]hexane 3,3-dioxide* (**4**). $C_7H_{12}O_2S$; Mr = 160.24; monoclinic, $P2_1/c$; a = 16.702 (1) Å, b = 9.232 (1) Å, c = 16.286 (3) Å, β = 108.12 (1)°; V = 2387 (1) Å$^3$; Z = 12; $D_x$ = 1.34 g/cm$^3$; λ(Mo Kα) = 0.71073 Å; μ = 3.3 cm$^{-1}$; F(000) = 1032; T = 173 ± 1 K. Colorless plate, 0.28 x 0.24 x 0.08 mm, mounted on a glass fiber, Enraf-Nonius CAD4 diffractometer, graphite monochromator, the ω-θ scan technique with an ω:θ scan speed ratio of 1.500 to 1, backgrounds obtained from analysis of the scan profile[26], unit cell constants from the setting angles of 25 reflections in the range 10 < θ < 14°, empirical absorption correction (from 0.889 to 1.000 on I), maximun 2θ = 52.0°, 0 < h < 20; 0 < k < 11; -19 < l < 18, anisotropic decay (from 0.862 to 1.057 on I), reflection averaging R(int) = 3.0%, 3565 total reflections measured, 3224 unique, 2671 reflections with $Fo^2 > 3.0\sigma(Fo^2)$, solution by direct methods (MULTAN[27]) refinement by full-matrix least-squares, function minimized was $\Sigma w(|Fo|-|Fc|)^2$, weight w is defined as 4 $Fo^2/\sigma^2(Fo^2)$, hydrogen atoms refined as riding atoms, 307 refined parameters, R = 0.056, wR = 0.074, S = 2.26, largest shift = 0.03σ, high peak in final difference map 0.90 (8) e/Å$^3$, low peak -0.14 (8) e/Å$^3$. Scattering factors for neutral atoms and the values for Δf' and Δf'' were taken from International Tables for X-ray Crystallography[28]; computer programs MolEN[29]. There are three independent molecules in the asymmetric unit, one of which is disordered. The disorder has been modelled as two superimposed molecules with population of 0.5 related by a twofold rotation about the S3C-C6C bond.

Single Crystal X-ray diffraction of *6,11-dimethylidene-3-thiatetracyclo[5.3.1.0$^{1,5}$.0$^{5,10}$]undec-8-ene 3,3-dioxide* (**12**). $C_{12}H_{12}O_2S$; Mr = 220.29; orthorhombic, Pccn; a = 25.122 (4) Å, b = 9.974 (2) Å, c = 8.153 (1) Å, V = 2043 (1) Å$^3$; Z = 8; $D_x$ = 1.43 g/cm$^3$; λ(Mo Kα) = 0.71073 Å; μ = 2.8 cm$^{-1}$; F(000) = 928; T = 95 ± 1 K. Colorless plate, 0.38 x 0.26 x 0.11 mm, mounted on a glass fiber, Enraf-Nonius CAD4 diffractometer, graphite monochromator, θ-2θ scan technique, unit cell constants from the setting angles of 25 reflections in the range 11 < θ < 14°, empirical absorption correction (from 0.972 to 0.997 on I), maximum 2θ = 52.0°, 0 < h < 30; 0 < k < 12; 0 < l < 10; linear decay (from 0.893 to 1.237 on I), reflection averaging R(int) = 1.9%, 2455 total reflections measured, 2330 unique 625 unobserved reflections, 1374 reflections with $Fo^2 > 3.0\sigma(Fo^2)$, solution by direct methods[27], refinement by full-matrix least-squares, function minimized was $\Sigma w(|Fo|-|Fc|)^2$, weight w is defined as 4 $Fo^2/\sigma^2(Fo^2)$, hydrogen atoms located and refined isotropically, 184 refined parameters, R = 0.037, $R_w$ = 0.045, S = 1.35, largest shift = 0.01 σ, high peak in final difference map 0.31 (7) e/Å$^3$, low peak -0.42 (7) e/Å$^3$. Scattering factors for neutral atoms and the values for Δf' and Δf'' were taken from International Tables for X-ray Crystallography[28]; computer programs MolEN[29].

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