151. Synthesis and Formation of Ironcarbonyl Complexes of 3′,3′-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane]. Single-Crystal and Molecular Structure of *syn, exo*^{2,3}-*anti, endo*^{5,6}-*trans*-μ-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*)-*C*,2,3,*C*-η:*C*,5,6,*C*-η-(3′,3′-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane])]bis(tricarbonyliron)[1])

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(17.VII.87)

The 3′,3′-dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane] (**3**) was derived from 6,6-dimethylfulvene and maleic anhydride. Its reaction with 1 equiv. of ethylenetetracarbonitrile (TCNE) was not regioselective and gave a 1:1 mixture of the corresponding monoadducts **10** and **11**. The rate constants of the *Diels-Alder* additions of **10** and **11** to TCNE were significantly smaller than that of the reaction **3** + TCNE. Monocomplexation of **3** with $Fe_2(CO)_9$ was highly *exo*-face selective giving a mixture of the corresponding monocomplexes **12** (*anti-exo*) and **13** (*syn-exo*). The latter were complexed with $Fe_2(CO)_9$ in a non-stereoselective fashion, giving mixtures of the dicomplexes **14** (*anti-exo, syn-endo*), **15** (*anti-exo, syn-exo*), and **16** (*anti-endo, syn-exo*). Exchange of the CO ligands was a faster process for the *endo*-$Fe(CO)_3$ moieties than for the *exo*-$Fe(CO)_3$ moieties. Line-shape analysis of the ^{13}C-NMR spectrum of **15** established that one of the *exo*-$Fe(CO)_3$ groups in **15** rotates *ca.* 3 times as fast as the other $Fe(CO)_3$ group at 40°. The structure of the *anti-endo, syn-exo* dicomplex **16** was determined by single-crystal X-ray diffraction studies.

Introduction. – The chemical and spectroscopic properties of the diene in 2,3-dimethylidene- and 2,3,5,6-tetramethylidenebicyclo[2.2.*n*]alkanes can be affected by remote substitution of the bicyclic skeleton [2]. In particular, we have shown recently that an acetal function attached at one of the bridgehead centres of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**1**) can induce stereo- and regioselective reactions for the two successive *Diels-Alder* additions to non-symmetrical dienophiles [3]. In the case of the 7,8-epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**2**), we had shown that the epoxide moiety led to a differentiation of the *Diels-Alder* reactivity of the two diene moieties. We found that ethylenetetracarbonitrile (TCNE) prefers to add onto the diene *syn* with respect to the oxirane [4]. We now report on the synthesis of a new type of epoxy-tetraene **3**. In the latter, the oxirane ring is in the mirror plane of the tetraene, a relative orientation which is perpendicular to that of the epoxide in **2**. We shall present our preliminary studies on the *Diels-Alder* reactivity of **3** and on its complexation with $Fe_2(CO)_9$. We have

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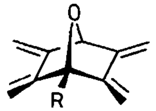
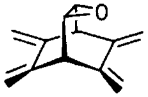
[1]) Interaction between non-conjugated chromophores, Part 27. Part 26, see [1].

[2]) Part of the planned Ph. D. thesis of *A. Rubello*, Université de Lausanne.



1 R = CH(OMe)$_2$
19 R = H



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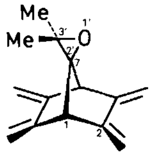
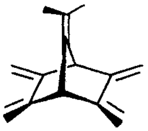


3

found that monocomplexation of **3** prefers the *exo* face of both diene moieties. This stereoselectivity was not observed for the double complexations of the tetraene.

Results and Discussion. – Our starting material for the synthesis of **3** is the tetrachloride **5**, a precursor of 7,7-dimethyl[2.2.1]hericene (**4**) [5]. It was derived in four steps from 6,6-dimethylfulvene and maleic anhydride. On attempting to prepare the corresponding ketone **6** by ozonolysis of **5**, we found that only the epoxide **7** was formed in 92% isolated yield. The same product was also obtained on oxidizing **5** with *m*-chloroperbenzoic acid in CHCl$_3$. A survey of the literature shows that ozonolysis of polysubstituted or/and sterically hindered alkenes can yield the corresponding epoxides instead of the expected ketone [6].



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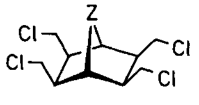
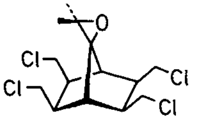


5 Z = C=CMe$_2$
6 Z = C=O



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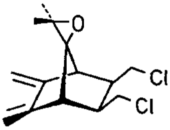

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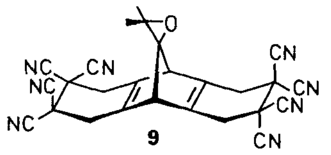
On treatment of **7** with an excess of *t*-BuOK in THF (70°, 5 equiv.), a mixture of diene **8** and tetraene **3** was formed in low yield. A good yield (69%) of **3** was obtained on heating **7** to 120° for 7 days in DMF/HMPT 6:1 in the presence of a *ca.* 20-fold excess of anhydrous CsF [7]. When heated to 120° for 2 h only in DMF/HMPT 8:1 in the presence of 1 equiv. of Cs$_2$CO$_3$ and 10 equiv. of CsF, incomplete elimination of HCl was observed and the diene **8** was isolated in 48% yield. Unfortunately, the configuration at C(7) in **8** could not be established unambiguously. It is interesting to note, however, that only one of the two possible conjugated dienes that can be formed from **7** has been isolated.

The structure of **3** was established unambiguously from its mode of formation, by its elemental analysis, and by its spectral data (see *Exper. Part*). It was confirmed by its *Diels-Alder* addition to TCNE. In the presence of 2 equiv. of the dienophile (acetone, 20°, 12 h), the corresponding bis-adduct **9** was formed (91%, isolated). When only 1 equiv. of TCNE was used, a 55:45 or 45:55 mixture of the mono-adducts **10** and **11** was obtained. Contrary to the cycloaddition of the epoxy-tetraene **2** to TCNE which was shown to prefer the diene unit *syn* with respect to the epoxide ring, the reaction **3** + TCNE was not regioselective. This indicates the absence of homoconjugative interactions between the epoxide and the tetraene moieties which were invoked to interprete the *Diels-Alder* reactivity of **2** [4]. Indeed, an eventual HOMO(*'anti'*-diene) – LUMO(epoxide) as that invoked in **2** [4] cannot intervene in **3** for reasons of symmetry. There was no trace of **9** in the reaction of **3** with 1 equiv. or less of TCNE, thus showing that the rate constant of the addition of the 1st equiv. of dienophile is significantly larger than that of the addition of the 2nd equiv. This property is typical of all the exocyclic tetraenes grafted onto bicyclo[2.2.1]heptane skeletons reported so far [2] [5] [8].



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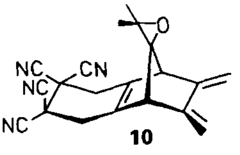

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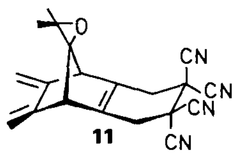

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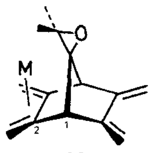
On heating **3** in MeOH in the presence of 12 equiv. of $Fe_2(CO)_9$, a 8:7 mixture of the monocomplexes **12** (*anti-exo*) and **13** (*syn-exo*) was formed after 1 h (15% of conversion of **3**)[3]). After 2.5 h at 65°, a 3:2.5:1.5:1:1.5 mixture **12/13/14/15/16** was observed (35% of conversion). On further heating, the monocomplexes **12** and **13** disappeared in favour of the dicomplexes **14–16**. When pure **13** was heated with $Fe_2(CO)_9$ in MeOH, a 2:1 mixture **15/16** was formed, with no trace of **14**. Similarly, when pure **12** was treated with $Fe_2(CO)_9$, a 1:1 mixture **14/15** was obtained, with no trace of **16**. We could not detect the formation



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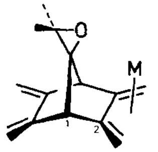

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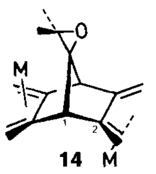

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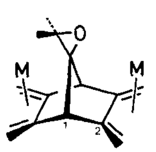

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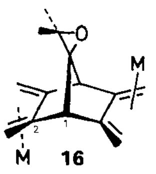

16

M = $Fe(CO)_3$

of monocomplexes **17** (*anti-endo*) and **18** (*syn-endo*) with the $Fe(CO)_3$ moiety in the *endo* face of the diene units. Thus, the monocomplexation of **3** with $Fe_2(CO)_9$ in MeOH appears to be *exo*-face-selective, both diene moieties being complexed with similar rates[4]). In the light of this observation, competitive formation of **15** with **16** on treating **13** with $Fe_2(CO)_9$ and of **14** with **15** on treating **12** with $Fe_2(CO)_9$ is a surprise. We do not have yet an explanation to offer to explain the *exo*-face selectivity for the monocomplexation of **3** while there is no such selectivity for the coordination of the second $Fe(CO)_3$ units. It should be noted here that the pure complexes **12–16** were stable after prolonged heating in MeOH. The proportions of complexes **12–16** formed under the above conditions correspond to those of kinetic control.

The structures of **12–16** were given by their mode of formation, their elemental analysis and their spectral data. The *exo* configuration of the $Fe(CO)_3$ moieties in the monocomplexes **12** and **13** was established by their 360-MHz ^1H-NMR spectra that

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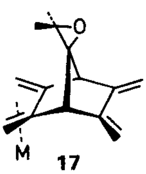
[3]) The configurational prefixes *syn* and *anti* are used to indicate that the Fe-atom is on the same and opposite side, respectively, as the O-atom with respect to the plane defined by the two bridgeheads and the bridge atom.

[4]) Coordinations of 2,3-dimethylidene-7-oxabicyclo[2.2.1]heptane with $Fe_2(CO)_9$ in MeOH [9] and of 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane with $Fe_2(CO)_9$ in Et_2O/pentane were also *exo*-face-selective [10]. In the cases of 2,3-dimethylidenebicyclo[2.2.1]heptane, 5,6-dimethylidenebicyclo[2.2.1]hept-2-ene [11] [12], and 7,7-dimethoxy-2,3-dimethylidenebicyclo[2.2.1]heptane [13], both faces of the diene moieties were complexed with similar rates with $Fe_2(CO)_9$ in MeOH.



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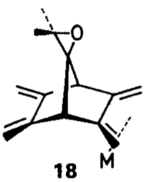

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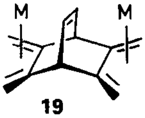

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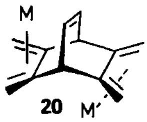

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M = $Fe(CO)_3$

showed typical long-range coupling constants of *ca.* 0.4 Hz between the bridgehead protons H–C(1), H–C(4) and the protons *trans* with respect to C(2), C(3) of the methylidene group attached to the *exo*-metal atom. Such long-range coupling was not observed for *endo* complexes [9]. On coordination of the exocyclic butadiene moiety to $Fe(CO)_3$, the H-atoms of the methylidene group *trans* with respect to C(2), C(3) are bent toward the *exo* face by *ca.* 15°, thus making them almost aligned with the adjacent bridgehead C–H bonds (M type of ^4J(H,H) coupling). In the case of an *endo* diene-$Fe(CO)_3$ complex, the dihedral angle between these C–H bonds is larger than 35°, thus rendering the corresponding ^4J(H,H) coupling near zero [10] [14].

The distinction between **12** and **13** was based on their reactivity toward $Fe_2(CO)_9$ (see above). The energy barrier for the rotation of the $Fe(CO)_3$ tripod in tricarbonyl(diene)iron complexes grafted onto bicyclo[2.2.1]heptane skeletons never exceeds 13 kcal/mol [15] which leads to the observation of coalesced signals in the ^{13}C-NMR spectrum of the $Fe(CO)_3$ C-atoms at 25° (see *e.g.* [11–13]). Both ^{13}C-NMR spectra of **12** and **13** showed 2 pairs of carbonyl signals at 25°. At 75°, **12** was decomposed slowly. At that temperature, the ^{13}C-NMR spectrum of **12** showed 2 signals at 213.8 (1 C) and 209.5 ppm (2 C) that had not coalesced yet. Similarly, no coalescence of the 2 carbonyl *s* at 215.0 (1 C) and 208.9 ppm (2 C) could be seen by recording the ^{13}C-NMR spectrum of **13** at 85°, temperature at which decomposition of the complex occurred. In that case, the rotation of the *exo*-$Fe(CO)_3$ tripod is a very slow process because of the bulk of the oxirane ring.

The ^1H-NMR spectrum of **15** showed a ^4J(H,H) of *ca.* 0.4 Hz between the bridgehead protons H–C(1), H–C(4) and both type of methylidene protons *trans* with respect to C(2), C(3) and C(5), C(6), thus confirming the *exo* configuration of both $Fe(CO)_3$ moieties. In contrast, the ^1H-NMR spectra of **14** and **16** showed this long-range coupling constant for only one of the two tricarbonyl(diene)iron moieties. At 25°, the ^{13}C-NMR spectrum ($CDCl_3$) of **16** showed 2 sharp *s* at 214.8 (1 C) and 208.8 (2 C) ppm for the $Fe(CO)_3$ moieties. At −88°, 2 other *s* at 215.4 (1 C) and 209.2 (2 C) ppm were visible. The former pair of signals were attributed to the *exo*-$Fe(CO)_3$ moiety whereas the latter belong to the *endo*-$Fe(CO)_3$ unit by virtue of steric hindrance which blocks the rotation of the *exo*-$Fe(CO)_3$ tripod, but not as much that of the *endo*-$Fe(CO)_3$ tripod. The ^{13}C-NMR spectrum of **14** measured at 25° (as for **16**) showed 2 signals at 213.8 (1 C) and 209.2 (2 C) ppm. At −88°, the ^{13}C-NMR spectrum of **14** displayed another pair of signals at 209.3 (1 C) and 213.8 (2 C) ppm attributed to the more slowly rotating *endo*-$Fe(CO)_3$ tripod. Distinction between structures **14** and **16** was established by X-ray single-crystal diffraction studies on **16** (see *Exper. Part*).

The ^{13}C-NMR spectrum of **15** measured at 25° displayed 2 sharp signals at 215.0 (1 C) and 208.7 (2 C) ppm and 2 broader *s* at 214.0 (1 C) and 209.4 (2 C) ppm (see *Fig. 1*). At higher temperatures, line broadening for all 4 signals was observed. Line-shape analysis of these signals allowed one to estimate the rate constans k_1 and k_2 for both exchange

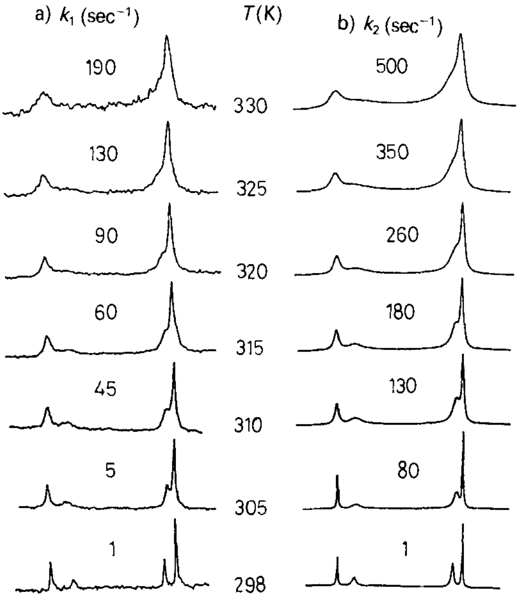

Fig. 1. a) *Observed and* b) *simulated* [18] *^{13}C-NMR spectrum of dicomplex* **15** (*syn-exo, anti-exo*) *as a function of temperature*

processes as a function of temperature. These data showed that one of the Fe(CO)$_3$ tripod is exchanging the CO signals *ca.* 3 times as fast as the other at 42° (see *Fig. 1*). This result suggests, thus, that the bulk of the dimethyl-substituted C-atom of the epoxide moiety does not affect in a significant fashion the rotation rate of the *exo*-Fe(CO)$_3$ group as compared with the effect of the O-atom in **15**.

The ^{13}C-NMR chemical shift of the gem-dimethyl groups in **3** is 20.9 ppm. For complexes **13** and **16** in which there is no *anti-exo*-Fe(CO)$_3$ group, the δ_C(Me) are nearly the same (20.8 ppm for **13**, 20.8 ppm for **16**) as in **3**. In contrast, for complexes **12**, **14**, and **15** in which there is an *anti-exo*-Fe(CO)$_3$ group, a small deshielding effect is observed (21.8 ppm for **12**, 21.5 ppm for **14**, and 21.7 ppm for **15**) for the gem-dimethyl C-atoms.

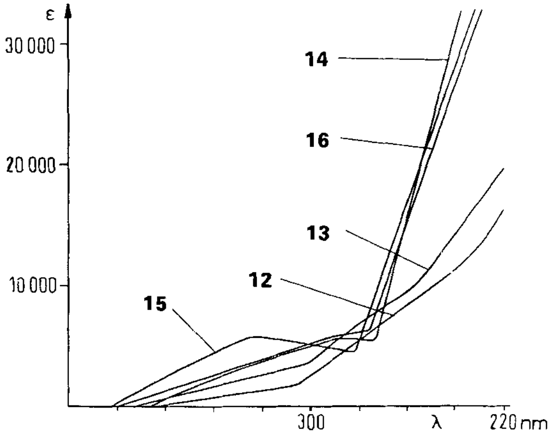

Fig. 2. *UV/VIS spectra of monocomplexes* **12** *and* **13** *and of dicomplexes* **14**–**16** *in isooctane*

The UV/VIS spectra of **12**–**16** are reproduced in *Fig. 2*. They are almost featureless. Nevertheless, it is interesting to note that the final absorption at 210 nm of the dicomplexes **14**–**16** is about the same and is twice as intense as that of the monocomplexes **12** and **13**. More interesting are the absorptions between 300 and 380 nm. While the monocomplexes **12** and **13** and the dicomplexes **14** and **16** have similar intensities in the latter region, that of the dicomplex **15** is definitively higher, showing a maximum at *ca.* 315 nm. This observation suggests a through-space interaction between the two tricarbonyl(diene)iron chromophores in **15**. The latter is possible only in the *exo,exo* dicomplex **15** and not in the *endo,exo* dicomplexes **14** and **16**. A similar observation had been made by comparing the UV/VIS spectra of the dicomplexes **19** and **20**[5]) [16].

We thank *F. Hoffmann-La Roche & Co. AG*, Basel, the *Swiss National Science Foundation*, and the *Fonds Herbette*, Lausanne, for generous support.

Experimental Part

General. See [1] [3].

2-exo,3-exo,5-exo,6-exo-*Tetrakis(chloromethyl)3′,3′-dimethylspiro[bicyclo[2.2.1]heptane-7,2′-oxirane]* (**7**). Ozone (3%) in O_2, 1000 cm^3/min, was bubbled through a soln. of **5** (2.3 g, 6.97 mmol) in AcOEt (70 ml) cooled to −20° for 3 h. After warming to 20°, the solvent was evaporated. The yellowish residue was dried (P_2O_5) *in vacuo*. The crude crystalline **7** was recrystallized from CH_2Cl_2/hexane 2:1, yielding 2.2 g (92%) of colourless crystals, slightly hygroscopic. M.p. 75–77°. IR (KBr): 3020, 2970, 2950, 1730, 1445, 1315, 1290, 1260, 1185. ^{1}H-NMR ($CDCl_3$): 1.28 (*s*, 2 Me); 2.23 (*s*, H–C(1), H–C(4)); 2.4 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)); 3.5 (*m*, 4 CH_2Cl). ^{13}C-NMR ($CDCl_3$): 78.4 (br. *s*, C(7)); 58.5 (br. *s*, C(3′)); 49.3 (*d*, ^1J(C,H) = 140, C(5), C(6)); 46.1 (*d*, ^1J(C,H) = 141, C(2), C(3)); 44.5 (*d*, ^1J(C,H) = 146, C(1), C(4)); 43.4, 42.6 (2*t*, ^1J(C,H) = 150–152, 4 $ClCH_2$); 22.3 (*qq*, ^1J(C,H) = 128, ^3J(C,H) = 3, 2 Me). MS (70 eV): 346 (30, $M^{+\cdot}$), 331 (9), 311 (10), 295 (58), 267 (58), 253 (87), 237 (23), 219 (34), 203 (18), 189 (18), 179 (51), 163 (34), 143 (23), 127 (44), 117 (32), 103 (36), 91 (100), 77 (75), 65 (61), 59 (48), 53 (39). Anal. calc. for $C_{14}H_{20}Cl_4O$ (346.13): C 48.58, H 5.83; found: C 48.49, H 5.79.

2-exo,3-exo-*Bis(chloromethyl)-3′,3′-dimethyl-5,6-dimethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane]* (**8**). A mixture of **7** (92 mg, 0.265 mmol), Cs_2CO_3 (87 mg, 0.265 mmol), and anh. CsF (405 mg, 2.6 mmol; dried in a flame) in DMF/HMPT 8:1 (4.5 ml) was heated to 120° under Ar for 2 h. After cooling to 20°, H_2O (5 ml) and CH_2Cl_2 (10 ml) were added. The aq. layer was extracted with CH_2Cl_2 (50 ml, 3 times). The combined org. extracts were washed with brine (150 ml, 5 times), dried ($MgSO_4$), and evaporated, and the residue was purified by column chromatography on *Florisil* (19 g, hexane): 35 mg (48%) of colourless crystals. M.p. 93–95° (hexane). UV (95% EtOH): 257 (sh, 6040), 248 (9470), 241 (sh, 8180), 229 (sh, 4500). UV (isooctane): 257 (sh, 6250), 248 (9470), 211 (sh, 8180), 228 (sh, 4140). IR ($CHCl_3$): 3060, 2950, 1280, 910. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 2 Me); 2.53 (*m*, H–C(2), H–C(3)); 2.68 (*s*, H–C(1), H–C(4)); 3.78 (*m*, 2 $ClCH_2$); 4.77, 5.28 (2*s*, CH_2=C(5), CH_2=C(6)). ^{13}C-NMR ($CDCl_3$): 146.6 (*s*, C(5), C(6)); 103.0 (*t*, ^1J(C,H) = 160, *C*H_2=C(5), *C*H_2=C(6)); 79.0 (*s*, C(7)); 58.1 (*s*, C(3′)); 50.0 (*d*, ^1J(C,H) = 142, C(1), C(4)); 48.9 (*d*, ^1J(C,H) = 142, C(2), C(3)); 43.2 (*t*, ^1J(C,H) = 154, 2 $ClCH_2$); 21.2 (*qd*, ^1J(C,H) = 126, ^3J(C,H) = 4, 2 Me). MS (70 eV): 272 (5, $M^{+\cdot}$), 237 (3), 223 (8), 167 (14), 159 (24), 153 (14), 139 (100), 131 (10), 117 (18), 105 (17), 91 (22), 77 (13), 69 (16). Anal. calc. for $C_{14}H_{20}Cl_4O$ (272.34): C 61.75, H 6.66; found: C 61.43, H 6.39.

3′,3′-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane] (**3**). To **7** (13 g, 0.037 mol), DMF (600 ml), and HMPT (100 ml) freshly dried and distilled over CaH_2, in a flame-dried flask, CsF (100 g, 0.65 mol; dried in the flame) was added portionwise under stirring. After heating to 120° for 1 week, the mixture was cooled to 20° and H_2O (60 ml) added. The soln. was extracted with hexane/Et_2O 2:1 (150 ml, 4 times). The org. extracts were washed with brine (100 ml, 3 times), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (300 g SiO_2, CH_2Cl_2), yielding 5.1 g (69%) of colourless crystals. M.p. > 250° (dec.).

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[5]) For circular dichroism of tricarbonyliron mono- and dicomplexes of optically pure 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane derivatives, see [17].

Oxirane **3** is unstable and must be stored below –30°. UV (95% EtOH): 255 (sh, 7440), 237 (11300), 230 (11900), 222 (sh, 9800), 214 (sh, 7250). UV (isooctane): 277 (sh, 5900), 237 (8200), 229 (8960), 222 (sh, 7650), 215 (sh, 6210). IR ($CHCl_3$): 3100, 3000, 2980, 2940, 1780, 1680, 1630, 1460, 1410, 1380. ^{1}H-NMR ($CDCl_3$): 1.38 (*s*, 2 Me); 3.03 (*s*, H–C(1), H–C(4)); 4.93, 4.99, 5.24, 5.31 (4*s*, 4 CH_2=C). ^{13}C-NMR ($CDCl_3$): 146.6, 145.7 (2*s*, C(2), C(3), C(5), C(6)); 103.7, 102.9 (2*t*, ^{1}J(C,H) = 160, 4 *C*H_2=C); 79.9 (*s*, C(7)); 62.4 (*s*, C(3')); 55.8 (*dm*, ^{1}J(C,H) = 157, C(1), C(4)); 20.9 (*dq*, ^{1}J(C,H) = 138, ^{3}J(C,H) = 4, 2 Me). Anal. calc. for $C_{14}H_{16}O$ (200.32): C 83.95, H 8.05; found: C 83.90, H 7.99.

3,3-Dimethylspiro[oxirane-2,15'-tetracyclo[6.6.1.0^{2,7}*.0*^{9,14}*]pentadeca-2'(7'),9'(14')-diene]-4',4',5',5',11',11',12',12'-octacarbonitrile* (**9**). A mixture of **9** (100 mg, 0.5 mmol), TCNE (128 mg, 1 mmol), and acetone (5 ml) was stirred at 20° for 12 h. After addition of a few drops of pentane, the mixture was cooled to –10°. Yield 207 mg (91%), colourless crystals. M.p. > 250° (dec.). IR (KBr): 3000, 2980, 2920, 1720, 1640, 1440, 1380, 1230, 1220, 1190, 1140, 1070, 980, 900, 840. ^{1}H-NMR (CD_3COCD_3): 3.85 (*s*, H–C(1'), H–C(8')); 3.77 (*m*, CH_2(3'), CH_2(6'), CH_2(10'), CH_2(13')); 1.27 (*s*, 2 Me). Anal. calc. for $C_{26}H_{16}N_8O$ (456.470): C 68.41, H 3.53; found: C 68.58, H 3.83.

Tricarbonyliron Complexes of **3**. A mixture of **3** (2.8 g, 14 mmol), MeOH (300 ml), and $Fe_2(CO)_9$ (8 g, 24 mmol) was heated under reflux for 4 h. After addition of $Fe_2(CO)_9$ (5 g, *ca.* 15 mmol), the heating was continued for 5 h. After solvent evaporation, the residue was taken with hexane (300 ml), and acidic alumina (type I, 100 g) was added (decomposition of $Fe_3(CO)_{12}$, the soln. becomes yellow). After filtration, the residue was washed with CH_2Cl_2 (200 ml) and the filtrate evaporated. The residue was fractionated by column chromatography (*Lobar Merk*, size *C*, *LiChroprep Si 60*, hexane/CH_2Cl_2 2:1, 15 ml/min). The following products were obtained successively: 1.2 g (18%) of **15**, 0.65 g (9%) of **16**, 0.68 g (10%) of **14**, 0.5 g (10%) of **13**, and finally 0.4 g (6%) of **12**.

anti,exo-*Tricarbonyl[(1*R*,2*R*,3*S*,4*S*)-C,2,3,C-η-(3',3'-dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2'-oxirane])]iron*[3][6] (**12**). Yellow crystals. M.p. 134° (dec.; hexane). UV (isooctane): 217 (17700), 245 (10450), 309 (2650; see *Fig. 2*). UV (95% EtOH): 204 (22800), 217 (19100), 245 (11200), 309 (2630). IR (KBr): 3000, 2040, 1990–1960*s*, 1460, 1360, 1240, 1200, 1120, 960, 900. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.48, 5.26 (2*s*, CH_2=C(5), CH_2=C(6)); 3.08 (*d*, *J* = 0.4, H–C(1), H–C(4)); 1.88 (*dd*, ^{2}J = 2.9, ^{4}J = 0.4, 2 H, H *trans* to C(2), C(3) of CH_2=C(2) and CH_2=C(3)); 1.34 (*s*, 2 Me); 0.33 (*d*, ^{2}J = 2.9, 2 H, H *cis* to C(2), C(3) of CH_2=C(2) and CH_2=C(3)). ^{13}C-NMR (90.55 MHz, $CDCl_3$, 25°): 213.8 (1 C, CO); 209.5 (2 C, CO); 145.8 (*s*, C(5), C(6)); 108.8 (*s*, C(2), C(3)); 106.1 (*t*, ^{1}J(C,H) = 160, CH_2=C(5), *C*H_2=C(6)); 84.4 (*s*, C(7)); 66.6 (*s*, C(3')); 52.6 (*d*, ^{1}J(C,H) = 154, C(1), C(4)); 33.0 (*t*, *J*(C,H) = 160, *C*H_2=C(2), *C*H_2=C(3)); 21.8 (*q*, ^{1}J(C,H) = 126, 2 Me). MS (70 eV): 340 (11, $M^{+\cdot}$), 312 (41), 284 (66), 256 (22), 226 (30), 188 (31), 170 (20), 115 (30), 84 (22), 56 (100). Anal. calc. for $C_{17}H_{16}FeO_4$ (340.162): C 60.03, H 4.74; found: C 59.91, H 4.68.

syn,exo-*Tricarbonyl[(1*R*,2*R*,3*S*,4*S*)-C,2,3,C-η-(3',3'-dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2'-oxirane])]iron*[3] (**13**). Yellow crystals. M.p. 165° (dec.; hexane). UV (isooctane): 217 (22100), 247 (13300), 258 (10300), 302 (3600; see *Fig. 2*). UV (95% EtOH): 217 (23600), 247 (13800), 258 (10500), 302 (3700). IR (KBr): 3010, 3000, 2040, 1980, 1360, 1260, 1220, 1165, 1080, 980, 900, 880. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.56, 5.46 (2*s*, CH_2=C(5), CH_2=C(6)); 3.06 (*d*, ^{4}J = 0.4, H–C(1), H–C(4)); 1.88 (*dd*, ^{2}J = 2.8, ^{4}J = 0.4, H *trans* to C(2), C(3) of CH_2=C(2) and CH_2=C(3)); 1.29 (*s*, 2 Me); 0.25 (*d*, ^{2}J = 2.8, 2 H, H *cis* to C(2), C(3) of CH_2=C(2) and CH_2=C(3)). ^{13}C-NMR (90.55 MHz, $CDCl_3$, 25°): 215.0 (*s*, 1 C, CO); 208.9 (*s*, 2 C, CO); 144.6 (*s*, C(5), C(6)); 107.0 (*s*, C(2), C(3)); 104.6 (*t*, ^{1}J(C,H) = 160, *C*H_2=C(5), *C*H_2=C(6)); 83.4 (*s*, C(7)); 60.5 (*s*, C(3')); 53.0 (*d*, ^{1}J(C,H) = 154, C(1), C(4)); 32.6 (*t*, ^{1}J(C,H) = 160, CH_2=C(2), *C*H_2=C(3)); 20.8 (*q*, ^{1}J(C,H) = 126, 2 Me). MS (70 eV): 340 (3, $M^{+\cdot}$), 312 (21), 284 (55), 256 (83), 228 (23), 226 (56), 188 (58), 115 (38), 84 (29), 56 (100). Anal. calc. for $C_{17}H_{16}FeO_4$ (340.162): C 60.03, H 4.74; found: C 59.67, H 4.71.

syn,endo^{2,3}-anti,exo^{5,6}-trans-*μ-[(1*R*,2*R*,3*S*,4*S*,5*S*,6*R*)-C,2,3,C-η:C,5,6,C-η-(3',3'-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2'-oxirane])]bis(tricarbonyliron)*[3][6] (**14**). Yellow crystals. M.p. 187° (hexane). UV (isooctane): 207 (43100), 276 (4700), 292 (4800; see *Fig. 2*). IR (KBr): 3000, 2040, 1995, 1960, 1940, 1460, 1440, 1380, 1200, 1170, 1120, 970, 950. ^{1}H-NMR (80 MHz, $CDCl_3$): 3.39 (*d*, ^{4}J = 0.4, H–C(1), H–C(4)); 2.33 (*d*, ^{2}J = 2.9, 2 H, H of CH_2=C(2), CH_2=C(3) *trans* to C(2), C(3) and *syn*[3] to the O-atom); 2.0 (*dd*, ^{2}J = 2.9, ^{4}J = 0.4, 2 H, H of CH_2=C(5), CH_2=C(6) *trans* to C(5), C(6) and *anti*[3] to the O-atom); 1.40 (*s*, 2 Me); 0.92, 0.57 (2*d*, *J* = 3.2, 4 H, H of 4 CH_2=C *cis* to C(2), (C3) and C(5), C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$, 25°): 213.9 (*s*, 1 C), 209.2 (*s*, 2 C); 115.8 (*s*, C(2), C(3)); 112.9 (*s*, C(5), C(6)); 101.2 (*s*, C(7)); 70.4 (*s*, C(3')); 50.8 (*d*, ^{1}J(C,H) = 154, C(1), C(4)); 37.0 (*t*, ^{1}J(C,H) = 160, CH_2=C(2), CH_2=C(3)); 33.7 (*t*, ^{1}J(C,H) = 160, *C*H_2=C(5), *C*H_2=C(6)); 21.5 (*qd*, ^{1}J(C,H) = 126, ^{3}J(C,H) = 4, 2 Me). MS (70 eV): 480 (8, $M^{+\cdot}$), 452 (21), 424 (67), 396 (16), 340 (100), 312 (94), 284 (25), 112 (47), 84 (34). Anal. calc. for $C_{20}H_{16}Fe_2O_7$ (480.04): C 50.04, H 3.36; found: C 50.03, H 3.35.

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[6] For a better understanding of the names of **12**–**16** concerning the configurations, *exo*/*endo* and *syn*/*anti*[3] prefixes have been added.

syn, exo^{2,3}-anti, exo^{5,6}-cis-*μ-[(1R,2S,3R,4S,5S,6R)-C,2,3,C-η:C,5,6,C-η-(3′,3′-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane)]bis(tricarbonyliron)*3)6) (**15**). Yellow crystals M.p. 170° (hexane). UV (isooctane): 216 (sh, 34300), 222 (34700), 284 (4700), 328 (5815; see *Fig. 2*). IR (KBr): 3000, 2040, 1980, 1950, 1480, 1430, 1380, 1200, 1150, 1110, 1070, 970, 950. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.06 (br. *s*, H–C(1), H–C(4)); 1.96, 1.87 (2*dd*, $^2J = 2.9$, $^4J = 0.4$, 4 H); 1.29 (*s*, 2 Me); 0.53, 0.37 (2*d*, $^2J = 2.9$, 4 H). ^{13}C-NMR (90.55 MHz, $CDCl_3$, 25°): 215.0 (*s*, 1 C); 214.0 (*s*, 2 C); 209.4 (*s*, 1 C); 208.7 (*s*, 2 C); 116.9, 114.7 (2*s*, C(2), C(3), C(5), C(6)); 89.9 (*s*, C(7)); 65.6 (*s*, C(3′)); 50.8 (*d*, ^1J(C,H) = 156, C(1), C(4)); 33.5, 32.1 (2*t*, ^1J(C,H) = 160); 21.7 (*qd*, ^1J(C,H) = 126, ^3J(C,H) = 4, 2 Me). MS (70 eV): 480 (10, $M^{+\cdot}$), 452 (4), 424 (36), 368 (22), 340 (40), 312 (100), 284 (76), 256 (15), 188 (21), 112 (41). Anal. calc. for $C_{20}H_{16}Fe_2O_7$ (480.04): C 50.04, H 3.36; found: C 50.19, H 3.38.

syn, exo^{2,3}-anti, endo^{5,6}-trans-*μ-[(1R,2R,3S,4S,5S,6R)-C,2,3,C-η:C,5,6,C-η-(3′,3′-Dimethyl-2,3,5,6-tetramethylidenespiro[bicyclo[2.2.1]heptane-7,2′-oxirane])]bis(tricarbonyliron)*3)6) (**16**). Yellow crystals. M.p. 155° (hexane). UV (isooctane): 225 (36600), 276 (sh, 5700), 287 (sh, 5700; see *Fig. 2*). IR (KBr): 3010, 2990, 2050, 2040, 2000, 1960, 1360, 1220, 1150. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.33 (*d*, $^4J = 0.4$, H–C(1), H–C(4)); 2.2 (*d*, $^2J = 2.9$, 2 H, H of CH_2=C(2), CH_2=C(3) *trans* to C(2), C(3) and *syn*3) to the O-atom); 1.94 (*d*, $^2J = 2.9$, 2 H, H of CH_2=C(5), CH_2=C(6) *trans* to C(5), C(6) and *anti*3) to the O-atom); 0.71, 0.42 (2*d*, $^3J \approx 3$, 4 H, H of 4 CH_2=C *cis* to C(2), C(3) and C(5), C(6)). ^{13}C-NMR (90.55 MHz, $CDCl_3$): 214.8 (*s*, 1 C); 208.8 (*s*, 2 C); 112.9, 110.4 (2*s*, C(2), C(3), C(5), C(6)); 51.1 (*d*, ^1J(C,H) = 154, C(1), C(4)); 35.8, 33.1 (2*t*, ^1J(C,H) = 160, 4 CH_2=C); 20.8 (*qd*, ^1J(C,H) = 126, ^3J(C,H) = 4, 2 Me). MS (70 eV): 480 (10, $M^{+\cdot}$), 452 (22), 396 (51), 312 (100), 284 (50), 256 (16), 188 (16), 128 (18), 56 (70). Anal. calc. for $C_{20}H_{16}Fe_2O_7$ (480.04): C 50.04, H 3.36; found: C 50.01, H 3.33.

Crystal Structure of **16**. A single crystal of **16** was obtained by slow recrystallization from hexane at 20°. Single-crystal diffraction intensities were collected on a *Enraf-Nonius-CAD-4* autodiffractometer. *Table 1* gives the crystallographic data and data-collection procedure [20]. Atomic scattering factors for neutral C, O, Fe, and H [21] and anomalous coefficients for Fe [22] were included in the structure-factor calculations. List of atomic parameters are given in *Table 2*. A list of anisotropic thermal displacement parameters (anisotropic per H-atoms) is given in *Table 3*. A perspective view of the molecular structure of **16** was prepared by the programm ORTEP [19] (*Fig. 3*). A list of the observed and calculated structure-factor amplitude are available on request from *G. C.*

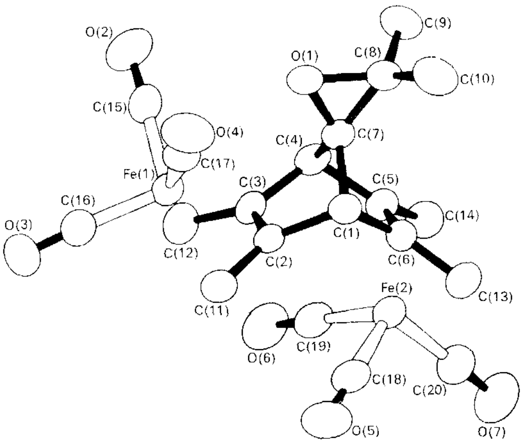

Fig. 3. *Perspective view of the molecular structure of* **16** (ORTEP program [19]). For reason of clarity, the H-atoms are not shown; the atom numbering does not correspond to the IUPAC numbering; atoms are reproduced with 50% thermal ellipsoids.

Table 1. *Crystal Data of* **16**, *Intensity Collection, and Refinement*

Formula	$C_{20}H_{16}O_7Fe_2$
Molecular mass	480.03
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	14.85(1)
b [Å]	8.753(1)
c [Å]	17.34(2)

Table 1 (cont.)

β [°]	115.56(8)
V [Å^3]	2033(4)
Z	4
d_{calc} (g cm^{-3})	1.57(1)
d_{obs} (g cm^{-3})	1.58(1)[a])
F_{000}	976
Radiation	MoK_α (graphite monochromator)
λ [Å]	0.71069
μ [cm^{-1}]	14.6
Crystal volume	$1.96 \cdot 10^{-3}$ cm^{-3}
Min/max transmission	0.66/0.78
Scan method	2θ–θ
Profile analysis	*Lehmann-Larsen (Schwarzenbach)* [20]
Scan width	$1.20° + 0.34 \text{ tg } \theta$
Scan speed	variable with intensity
$(\sin\theta/\lambda)_{max}$	0.60
Collected intensities	$\pm h + k \pm l$
Scattering factors	neutral atoms (*Cromer* and *Mann* [21])
Anomalous dispersion	Fe (*Cromer* and *Liberman* [22])
Observations	3579, of which 972 smaller than 3σ
Weights	$1/(\sigma^2 + 0.01F^2)$
Lattice constants	least-squares of 10 accurately centered reflections with $19° < 2\theta < 24°$
Thermal parameters	anisotropic for non-H-atoms, isotropic for H-atoms (H-atoms have been omitted on C(9) and C(10)[b])
Agreement factor	$R = 0.039$, $R_w = 0.064$
Error of an observation of unit weight	0.64
Observations per parameter	11.8
Largest shift error of refinement	0.04
Largest peak on a final *ΔF-Fourier*	0.59 e/Å^3
Refinement constants	soft restrictions on C–H bond distance (1 Å)
Resolution method	MULTAN [23] and *Fourier*
Refinement method	weighted block-diagonal least-squares (2 blocks)
Minimized quantity	$\Sigma w(F_o^2 - F_c^2) + \Sigma w'(d_p - d_c)^2$ (d_p: prescribed distance; d_c: calculated distance; $w' = 1/\sigma^2 = 100$)

[a]) By flotation in ZnI_2 solutions. [b]) See *Fig. 3* for atom numbering.

Table 2. *List of Atomic Parameters and Equivalent Temperature Factors for* **16**

Atom	x	y	z	U_{eq}
Fe(1)	0.28665(3)	0.44463(6)	0.41500(3)	0.0391(2)
Fe(2)	–0.04445(4)	0.18308(6)	0.36865(3)	0.0419(2)
O(2)	0.2953(3)	0.7796(4)	0.4169(3)	0.085(2)
O(3)	0.4747(2)	0.3688(5)	0.5601(2)	0.079(2)
O(4)	0.3418(3)	0.4506(4)	0.2713(2)	0.069(2)
O(5)	0.0958(3)	–0.0729(4)	0.4036(2)	0.072(2)
O(6)	0.0503(3)	0.2759(4)	0.5483(2)	0.073(2)
O(7)	–0.2140(3)	0.0170(5)	0.3719(3)	0.094(2)
C(15)	0.2903(3)	0.6494(5)	0.4157(3)	0.051(2)
C(16)	0.4025(3)	0.4006(5)	0.5024(3)	0.053(2)
C(17)	0.3187(3)	0.4459(4)	0.3265(3)	0.048(2)
C(18)	0.0424(3)	0.0284(5)	0.3887(3)	0.050(2)
C(19)	0.0141(3)	0.2416(5)	0.4775(3)	0.050(2)
C(20)	–0.1491(3)	0.0815(6)	0.3699(3)	0.061(2)

Table 2 (cont.)

Atom	x	y	z	U_{eq}
C(1)	0.0789(3)	0.3203(4)	0.2663(2)	0.037(1)
C(2)	0.1618(2)	0.3073(4)	0.3576(2)	0.035(1)
C(3)	0.1434(3)	0.4234(4)	0.4059(2)	0.037(1)
C(4)	0.0513(3)	0.5087(4)	0.3463(2)	0.039(1)
C(5)	-0.0378(3)	0.3967(4)	0.3185(2)	0.039(1)
C(6)	-0.0202(2)	0.2807(4)	0.2696(2)	0.038(1)
C(7)	0.0615(2)	0.4958(4)	0.2608(2)	0.036(1)
C(8)	0.0105(3)	0.5881(4)	0.1842(2)	0.046(1)
C(9)	-0.0481(3)	0.7276(5)	0.1852(3)	0.065(2)
C(10)	-0.0150(4)	0.5215(6)	0.0972(3)	0.068(2)
C(11)	0.2459(3)	0.2099(4)	0.3972(3)	0.047(2)
C(12)	0.2110(3)	0.4420(5)	0.4930(2)	0.051(2)
C(13)	-0.0907(3)	0.1610(5)	0.2348(3)	0.051(2)
C(14)	-0.1250(3)	0.3912(5)	0.3327(3)	0.053(2)
O(1)	0.1190(2)	0.5995(3)	0.2386(2)	0.045(1)
H(1)	0.098(3)	0.279(4)	0.222(2)	0.039(5)
H(2)	0.045(3)	0.611(2)	0.368(2)	0.033(5)
H(3)	0.265(3)	0.144(4)	0.359(2)	0.053(6)
H(4)	0.262(3)	0.173(5)	0.456(1)	0.057(6)
H(5)	0.189(3)	0.539(3)	0.510(3)	0.066(7)
H(6)	0.230(3)	0.340(3)	0.522(3)	0.074(7)
H(7)	-0.073(3)	0.070(3)	0.209(2)	0.045(6)
H(8)	-0.1645(7)	0.177(5)	0.208(3)	0.056(6)
H(9)	-0.188(2)	0.388(5)	0.279(1)	0.056(6)
H(10)	-0.117(3)	0.452(4)	0.384(2)	0.062(6)

Table 3. *Anisotropic Thermal Displacement Parameters* (anisotropic per H-atoms)

Atom	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.0362(3)	0.0411(4)	0.0390(3)	-0.0042(2)	0.0154(2)	-0.0004(2)
Fe(2)	0.0419(3)	0.0400(3)	0.0444(3)	-0.0082(2)	0.0191(2)	-0.0039(2)
O(2)	0.074(2)	0.047(2)	0.121(3)	-0.010(2)	0.032(2)	-0.018(2)
O(3)	0.051(2)	0.094(3)	0.068(2)	-0.011(2)	0.002(2)	0.028(2)
O(4)	0.091(2)	0.071(2)	0.065(2)	0.012(2)	0.053(2)	0.009(2)
O(5)	0.075(2)	0.054(2)	0.096(2)	0.011(2)	0.045(2)	0.011(2)
O(6)	0.091(2)	0.084(2)	0.052(2)	-0.029(2)	0.041(2)	-0.020(2)
O(7)	0.061(2)	0.110(3)	0.109(3)	-0.034(2)	0.036(2)	0.005(3)
C(15)	0.040(2)	0.053(3)	0.053(2)	-0.004(2)	0.014(2)	-0.009(2)
C(16)	0.043(2)	0.061(3)	0.051(2)	-0.011(2)	0.019(2)	0.006(2)
C(17)	0.047(2)	0.041(2)	0.054(2)	0.001(2)	0.021(2)	0.004(2)
C(18)	0.055(2)	0.046(2)	0.053(2)	-0.011(2)	0.028(2)	0.001(2)
C(19)	0.056(2)	0.050(2)	0.051(2)	-0.011(2)	0.030(2)	-0.004(2)
C(20)	0.049(2)	0.065(3)	0.068(3)	-0.011(2)	0.023(2)	0.003(2)
C(1)	0.044(2)	0.035(2)	0.032(2)	0.000(1)	0.017(1)	-0.004(1)
C(2)	0.036(2)	0.031(2)	0.037(2)	-0.005(1)	0.015(1)	-0.001(1)
C(3)	0.036(2)	0.042(2)	0.035(2)	-0.012(1)	0.017(1)	-0.005(1)
C(4)	0.047(2)	0.033(2)	0.043(2)	-0.004(2)	0.025(2)	-0.007(1)
C(5)	0.039(2)	0.039(2)	0.039(2)	-0.004(1)	0.016(1)	-0.003(1)
C(6)	0.038(2)	0.035(2)	0.035(2)	-0.001(1)	0.010(1)	-0.003(1)
C(7)	0.041(2)	0.032(2)	0.036(2)	-0.002(1)	0.018(1)	-0.003(1)
C(8)	0.051(2)	0.035(2)	0.044(2)	0.000(2)	0.015(2)	0.000(2)
C(9)	0.057(2)	0.040(2)	0.083(3)	0.015(2)	0.017(2)	*0.010(2)*

Table 3 (cont.)

Atom	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(10)	0.094(3)	0.066(3)	0.035(2)	0.003(3)	0.020(2)	0.004(2)
C(11)	0.047(2)	0.039(2)	0.053(2)	-0.001(2)	0.018(2)	0.000(2)
C(12)	0.048(2)	0.069(3)	0.041(2)	0.012(2)	0.023(2)	-0.009(2)
C(13)	0.057(2)	0.045(2)	0.044(2)	0.011(2)	0.015(2)	-0.009(2)
C(14)	0.044(2)	0.053(2)	0.064(3)	0.001(2)	0.025(2)	0.001(2)
O(1)	0.048(1)	0.040(1)	0.045(1)	0.003(1)	0.020(1)	0.007(1)
H(1)	0.039(5)					
H(2)	0.033(5)					
H(3)	0.053(6)					
H(4)	0.057(6)					
H(5)	0.066(7)					
H(6)	0.074(7)					
H(7)	0.045(6)					
H(8)	0.056(6)					
H(9)	0.056(6)					
H(10)	0.062(6)					

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