Synthesis of Stereoisomeric Ufolanes

Peter Boldt*[a], Eckart Arensmann[a], Martin Blenkle[a], Helmut Kersten[a], Heike Tendler[a], Rolf-Stefan Trog[a], Peter G. Jones*[b], and Detlev Döring[b]

Institut für Organische Chemie der Technischen Universität Braunschweig[a], Hagenring 30, W-3300 Braunschweig, F.R.G.

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig[b], Hagenring 30, W-3300 Braunschweig, F.R.G.

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Three of the six possible stereoisomers of dodecahydroacenaphthylene, *t,t,t*-ufolane (**1**), *c,c,t*-ufolane (**3**), and *c,c,c*-ufolane (**5**), have been synthesized for the first time. The configurations have been confirmed inter alia by an X-ray analysis of the precursors **11**, **14**, and **23** and the bromine adduct **24** of *c,c,c*-10-ufolene (**19**), the precursor of **5**.

The dodecahydroacenaphthylenes are of potential interest as fuel for aircraft and missiles in the speed range above Mach 3 (see for example refs.[1,2]). A mixture of stereoisomers has been obtained by reduction of acenaphthene (1,2-dihydroacenaphthylene) with hydrogen iodide[3], by catalytic hydrogenation[4,5,6] of acenaphthene or by acid-catalyzed rearrangement of 1,5,9-cyclododecatriene[7,8,9].

The names derived from the IUPAC nomenclature rules for the six possible stereoisomers **1** – **6** are quite long. Therefore, we propose the following simple notation: For the dodecahydroacenaphthylenes with *trans*-linkage of all rings, viz. for **1**, we have already proposed the name "ufolane"[10]. This name will now be used for *all stereoisomers of dodecahydroacenaphthylene*. For the notation of the configuration we follow the rules of Landa and Vanek[6]:

1. The molecules are drawn in such a way that the five-membered ring is at the top.

2. The hydrogen at the central tertiary carbon atom lies above the paper.

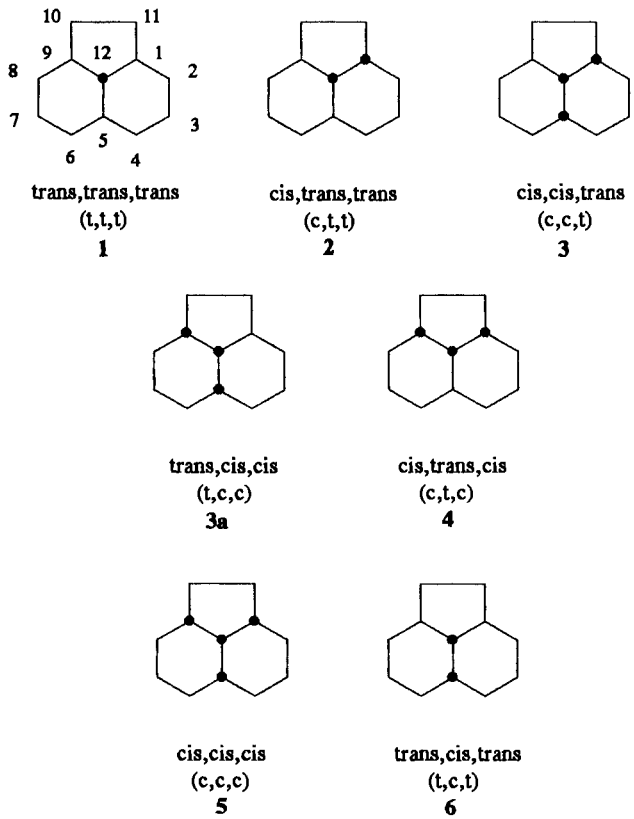
3. The relation of the carbon – hydrogen bond at the central tert. carbon atom to the carbon – hydrogen bonds at the other tert. carbon atom is characterized as *cis* or *trans*, beginning with C-1 (unsystematic numbering) and continuing clockwise.

4. In addition to the rules of Landa and Vanek[6] we propose: If there are two possibilities following rule 3 the direction is: *cis* precedes *trans*, e.g. the correct name for **3** will be *rac-cis,cis,trans*-ufolane or – abbreviated – *rac-c,c,t*-ufolane and not *rac-trans,cis,cis*-ufolane (*rac-t,c,c*-ufolane) as drawn in **3a**, if the racemate and not a specific enantiomer is to be indicated.

c,c,c-Ufolane (**5**) seems to be the most valuable isomer with respect to its use as a propellant because of its high mass density.

Vanek et al.[6] showed that five isomers are formed by catalytic hydrogenation of acenaphthene; the authors separated them by thermodiffusion and isolated one by preparative GC. The isomers were characterized by means of their GC retention indices[5,6]. Furthermore, the assignment of the structure of the five isomers was attempted on the basis of their ^{13}C-NMR spectra[11] or of the GC retention indices on columns with graphitized thermal carbon black[12]. However, an unequivocal structural assignment was still lacking. We describe here the synthesis of the three stereoisomers **1**, **3**, and **5**.

Scheme 1



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Synthesis of *c,c,c*-Ufolane (5)

A convenient preparation of **5** should be possible by reductive elimination of the vicinal hydroxy groups of the easily accessible[10] *trans*-10,11-dihydroxy-*c,c,c*-ufolane (**13**) to the new *c,c,c*-10-ufolene (**19**), followed by catalytic hydrogenation.

Jones and Thomson[13] describe e.g. the mild conversion of *vic*-diols via their mesylates by the reaction with iodide, but the reaction with the dimesylate of **13** failed. With iodide in the presence of zinc[14] several isomeric alkenes are formed as revealed by GC-MS analysis. The reductive elimination of the two hydroxy groups by means of the widely used method of McMurry[15] failed as well, only traces of **19** being formed. These results may be due to the fact that the ring system of **13**, especially the five-membered ring, is rigid and hence the dihedral angle between the two *trans*-hydroxy groups is too large. However, the *cis*-10,11-dihydroxy-*c,c,c*-ufolane **14** was converted into **19** in only 8% yield according to the McMurry method as modified by Lenoir[16]. The method of Garegg and Samuelson[17] for the reductive elimination of *trans*-diols was more successful: Heating of **13** with triphenylphosphane, iodine, and imidazole yielded 22% of **19**.

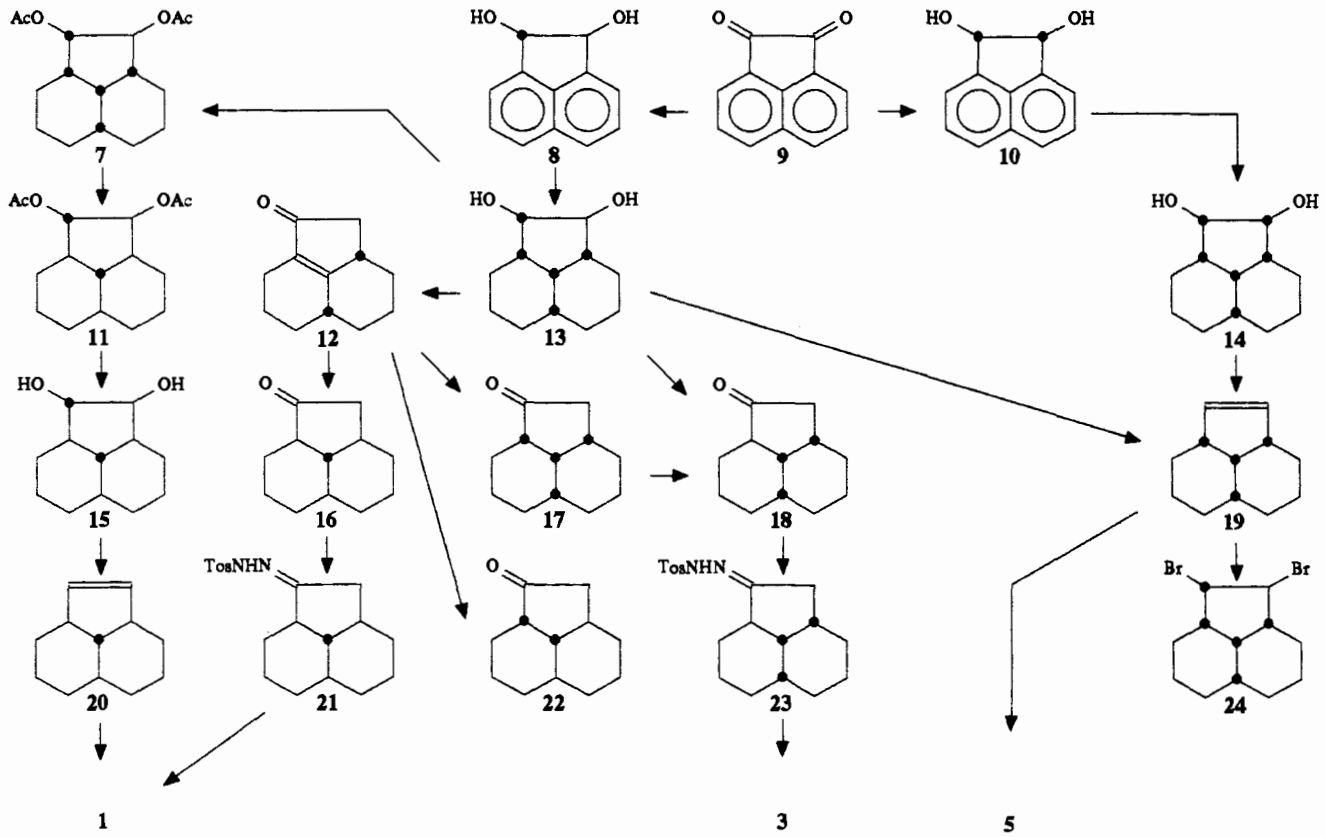
The structure of **13** has previously been established by an X-ray analysis[10]. The reductive elimination of the two hydroxy groups by the method of Garegg and Samuelson should not influence the configuration at C-1 and C-9[17]. Therefore, the reaction product is considered to be *c,c,c*-10-ufolene (**19**). Further evidence is derived from the fact that the double bond is not IR-active but Raman-active, that only seven signals are observed in the ^{13}C-NMR spectrum, and ultimately by the X-ray analysis of the product of bromine addition to **19**, which proved to be *trans*-10,11-dibromo-*c,c,c*-ufolane (**24**).

The *cis*-10,11-dihydroxy-*c,c,c*-ufolane **14** was obtained by catalytic hydrogenation of *cis*-1,2-dihydroxyacenaphthene (**10**). The structure was established by an X-ray analysis. It proved to be identical with one isomer reported in ref.[10]. Another *cis*-10,11-dihydroxyufolane (18%) was detected in the hydrogenation product and considered as the second *cis*-10,11-dihydroxy-*c,c,c*-ufolane (see ref.[10]).

trans-1,2-Dihydroxyacenaphthene (**8**) was prepared as previously described[10] by reduction of acenaphthenequinone (**9**) with $NaBH_4$ in tetrahydrofuran. The byproduct *cis*-1,2-dihydroxyacenaphthene (**10**) can be separated by recrystallization. For the preparation of **10** the reduction of **9** was performed in diethyl ether, because the *cis/trans* ratio was higher in this solvent.

Catalytic hydrogenation of **19** gave **5**, which possesses a plane of symmetry and therefore shows only seven signals in its ^{13}C-NMR spectrum. As a comparison of the ^{13}C-NMR data reveals, *c,c,c*-ufolane has already been isolated by Petrov[11] from a mixture of isomers obtained by hydrogenation of acenaphthene. But no description of the isolation procedure and of the structure elucidation is given[11] and the ref. mentioned[18] is not available.

Scheme 2



Synthesis of *c,c,t*-Ufolane (3)

The ufolenone **12** is a key intermediate in the stereoselective synthesis of *t,t,t*-10-ufolene (**20**)[10]. *trans*-Addition of hydrogen by reduction with lithium in ammonia gave *t,t,t*-10-ufolanone (**16**) with the desired ring configuration[10].

cis-Addition of hydrogen should lead in turn to *c,c,c*-10-ufolanone (**17**) or *t,t,c*-10-ufolanone (**22**) and could open the way for the synthesis of new ufolane isomers. However, upon catalytic hydrogenation the *cis*-addition from the convex side of the molecule, leading to **17**, is more probable and thus **17** was regarded initially as a possible intermediate for the synthesis of **5**.

Hydrogenation of **12** yielded two fractions after workup distillation. The first shows nearly the same mass spectrum as **20**[10], but in the ^{1}H-NMR spectrum no signals in the area of vinylic protons can be observed and in the ^{13}C-NMR spectrum eight signals of secondary, two of tertiary, and two of quaternary carbon atoms can be detected. These findings are only compatible with the structure of a 1(12)-ufolene (**25**), the formation of which under the reaction conditions cannot be rationalized.

The second fraction consists (as determined by a GC/MS analysis) of a 1:1 mixture of two ufolanones. On warming the mixture in dilute alkaline or acidic methanolic solution the peak of the compound with the longer retention time (capillary column, SE-30) vanishes gradually and the other peak becomes stronger. Our explanation is that **17** is formed as expected on hydrogenation and then is readily epimerized to the thermodynamically more stable *c,c,t*-10-ufolanone (**18**) under acidic or basic conditions or in part even upon distillation. The structure of **18** was established by an X-ray analysis of its tosylhydrazone **23**.

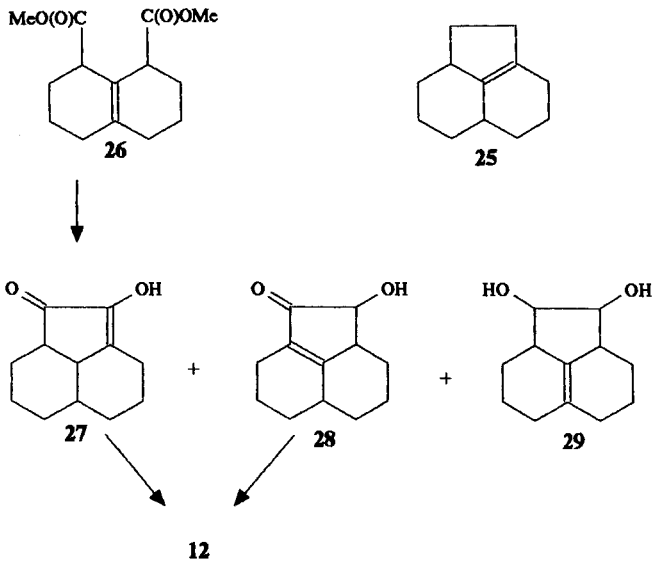
A simple two-step synthesis of **18** with an overall yield of 48% was carried out also by catalytic hydrogenation of 1-hydroxyacenaphthene followed by chromium trioxide oxidation.

Tosylhydrazones can be converted into the corresponding alkanes by reduction with $NaBH_4$[20]. In this way, **23** yielded directly the new *c,c,t*-ufolane (**3**). Its structure follows from the X-ray analysis of **23** and the assumption that in the reduction of the hydrazono group the adjacent CH bonds are not attacked[20]. As expected and in contrast to *c,c,c*-ufolane (**5**), **3** shows twelve ^{13}C-NMR signals.

Synthesis of *t,t,t*-Ufolane (1)

The synthesis of **1** should easily be accomplished by catalytic hydrogenation of *t,t,t*-10-ufolene (**20**). Compound **20** has already been prepared by an eight-step synthesis starting with dimethyl $\Delta^{9,10}$-octaline-1,8-dicarboxylate (**26**)[10]. One step of this synthesis consisted in the preparation of **27** with unknown configuration by intramolecular acyloin condensation of **26** accompanied by the reduction of the central double bond. This acyloin condensation has been repeated several times since then, and we have found that besides **27** another isomeric α,β-unsaturated hydroxy ketone is formed in varying ratios. As the ^{1}H- and ^{13}C-NMR spectra as well as the elemental analysis and the IR and mass spectra reveal, this isomeric ketone has the structure **28** (configuration also unknown). Compound **28** represents the expected product of the acyloin condensation of **26** with subsequent migration of the double bond in conjugation with the carbonyl group. Fortunately, however, both **27** and **28** could be reduced with hydrogen iodide to give the same unsaturated ketone **12** with the configuration shown in Scheme 2.

Scheme 3



From the reaction mixture of the acyloin condensation we further isolated minor amounts of a compound which, on the basis of spectral data and the elemental analysis, possesses structure **29**.

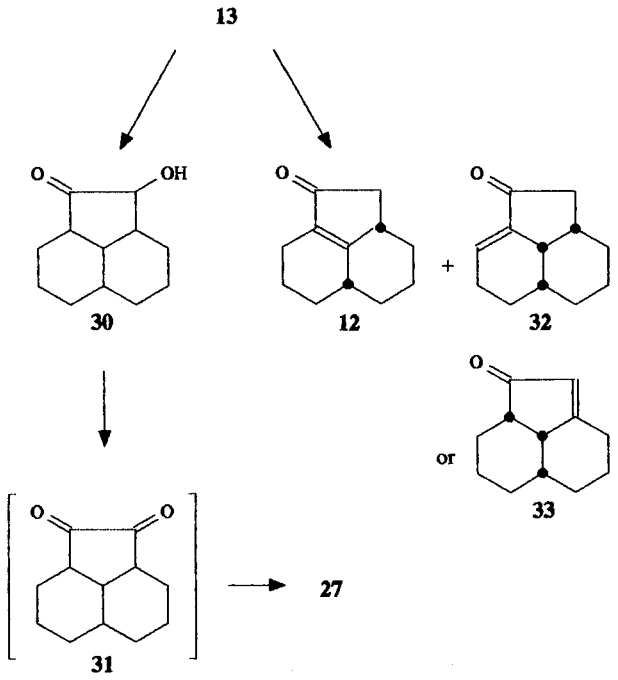
A much shorter synthesis of **27** should be possible by oxidation of the easily accessible **13** to give the diketone **31**, which in turn should tautomerize to **27**. The monoenol form is the more stable tautomer of 1,2-diketones of five-membered rings[21]. In the enolized diketone **27**, the two six-membered rings should be *cis*-connected, whereas **27**, obtained by acyloin condensation accompanied by reduction by sodium, probably has *trans*-fused rings. But the configuration is obviously established on reduction of **27** with hydrogen iodide and both stereoisomers should yield the same product with the required configuration, as shown in formula **12**.

α-Hydroxyketones can be oxidized to the corresponding diketones with cupric acetate[22], chromium(VI) oxide[23], or bismuth(III) oxide[24]. Thus, the conversion of **13** into the hydroxy ketone **30** by oxidation with silver carbonate[25] was first performed. However, the oxidation of **30** with cupric acetate or bismuth(III) oxide yielded mixtures, containing no **27**, whereas oxidation with chromium(VI) afforded carboxylic acids. Obviously, with chromium(VI) the oxidation did not stop at the diketone stage, probably because the spontaneously formed tautomeric enone is prone to further oxidation.

Vicinal diols have been dehydrogenated to α-diketones inter alia with tris(triphenylphosphane)ruthenium dichloride as catalyst and benzylidene acetone as hydrogen acceptor[16].

Surprisingly, treatment of **13** with these reagents did not furnished **31** or **27** but in good yield (73%) a 10:1 mixture of **12** and another α,β-unsaturated monoketone, either **32** or **33**. Reduction of the mixture with lithium in liquid ammonia[10] yielded a 5:1 mixture of **16** and **18**. Compound **16** is the product expected by *trans* addition of hydrogen to the double bond of **12**, as described earlier[10]. The occurrence of **18** can only be explained if it was formed from an α,β-unsaturated ketone that already possesses *cis* configuration at C-1, C-5, and C-12, as in **32**, or by addition of hydrogen at C-1 in **33** from its convex side and epimerization of the resulting **17**. Even more surprising was the fact that no benzylidene acetone was needed for the catalytic dehydrogenation of **13**. The result of the reaction was the same whether benzylidene acetone was present or not.

Scheme 4



Compounds **12** and **32/33** as well as **18** and **16** were separated by GC and identified or characterized by their retention times and/or spectral data. In the synthesis of **1**, the mixtures of the isomeric ketones **12** and **32/33** were reduced with lithium in liquid ammonia. The ketones **16** and **18** could be easily separated by recrystallization of their tosylhydrazones **21** and **23**. Reduction of **21** with $NaBH_4$ gave **1**. The overall yield of **1** in the simple four-step process starting from the easily accessible dihydroxyufolane **13** is 10%. The synthesis of *t,t,t*-10-ufolene (**20**), as described earlier[10], and subsequent hydrogenation to give **1** would have needed nine steps affording a lower yield.

A still simpler synthesis of **1** starting from **13** was achieved by a mercury-sensitized photochemical isomerization[26] of **7**, the diacetate of **13**, giving **11**. After hydrolysis to **15** the two hydroxy groups were reductively eliminated by using the method of Garegg and Samuelson[17] to furnish **20**, which in turn was converted into **1** by catalytic hydrogenation. The structure of **11** as *trans*-10,11-diacetoxy-*t,t,t*-ufolane was established by an X-ray analysis.

We also tried to isomerize 10,11-*trans*-dihydroxy-*c,c,c*-ufolane (**13**) directly by irradiation of its cyclohexane or ethanol solution with mercuric bromide as sensitizer, but no reaction took place. For the isomerization of hydrocarbons Kochi et al.[27,28] used acetone as solvent to prevent the precipitation of mercury on irradiation. Surprisingly, under these conditions **13** was converted into a mixture of products containing (GC) 48% of *c,c,t*-10-ufolanone (**18**) besides about 7% of another isomeric ufolanone and only 10% of **15** as revealed by a mass spectral analysis. Obviously under these conditions elimination of water took place, possibly with the formation of **17**, which in turn isomerized to **18**.

As further experiments showed, dehydration occured on irradiation even in the absence of mercuric bromide. But the reaction seems to be restricted to the diol **13**, since on irradiation of *trans*-1,2-dihydroxycyclopentane and *trans*-1,2-dihydroxycyclohexane in acetone no elimination of water was observed.

As expected from its symmetry, *t,t,t*-ufolane (**1**) shows only seven signals in its ^{13}C-NMR spectrum.

Ufolanes from Other Sources

a) Hydrogenation of Acenapthene

The catalytic hydrogenation of acenaphthene yielded five of the possible six ufolane isomers, which could be separated by gas chromatography on SE-30 GLC-capillary columns. The composition is listed in Table 1. Compounds No. 1, 3, and 5 could be identified by admixture of the pure isomers. The mixture was prepared under relatively mild conditions, i.e. by hydrogenation at 100°C/30 MPa with Raney nickel (activity grade W6). As expected, the *c,c,c*-isomer was formed predominantly, and apparently no substantial isomerization occured. Hydrogenation at 180–200°C/12 MPa yielded only 83.44% *c,c,c*-ufolane, which could be separated by preparative GC[5]; after heating to 300–340°C the composition was (compound no. in Table 1/%): 1/31.0; 2/1.5; 3/38.9; 4/27.7; 5/0.9[5]. Obviously, isomerization took place under these conditions and the composition of the products seemed to be not far from that of the equilibrium mixture expected on the basis of the calculated energies (MMX[31]).

Isomerization of the product mixture containing 94% of *c,c,c*-ufolane by mercury-sensitized irradiation[26] yielded a

Table 1. Ufolane isomers obtained by catalytic hydrogenation of acenaphthene. Percentages (%) as determined by GC, KI = Kovats index[29,30] at 150°C, boiling points estimated[29], MMX energies calculated by using the PC Model[31]

No.	Ufolane isomer	%	KI (this work)	KI ref.[33]	KI ref.[32]	b.p. [°C]	MMX energy
1	*t,t,t* **1**	0.8	1267	1274	1274	210	23.6
2	(*c,t,t*) **2**	2.6	1290	1300	1295	215	27.1
3	*c,c,t* **3**	2.4	1313	1320	1317	220	24.7
4	(*c,t,c*) **4**	<0.1	–	1325	1323	–	24.8
5	*c,c,c* **5**	94	1354	1353	1352	230	28.5
6	(*t,c,t*) **6**	–	–	1380	–	–	33.9

mixture containing (compound no. in Table 1/%): 1/25.4, 2/3.2, 3/34.0, 4/17.6, and 5/17.4. This composition did not change even after prolonged irradiation.

The *t,t,t*-configuration of compound no. 1 was also deduced from a systematic study of the gas chromatographic behaviour of tricyclic saturated hydrocarbons[32], and the configuration of compounds no. 1–5 from the evaluation of the ^{13}C-NMR spectral data[11] or from their retention times on glass capillary columns packed with graphitized thermal carbon black[12]. The *t,c,t*-configuration then remains for compound no. 6, only observed by Bredael[33]. These configurations have now been proven by us for compounds no. 1, 3, and 5.

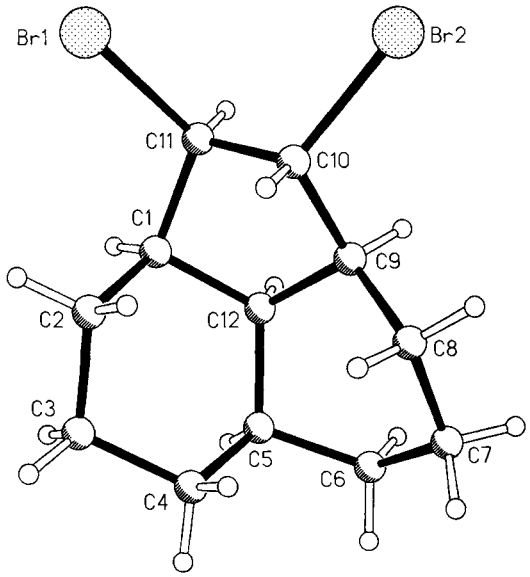


Figure 1. The molecule of compound **24** in the crystal. Radii are arbitrary

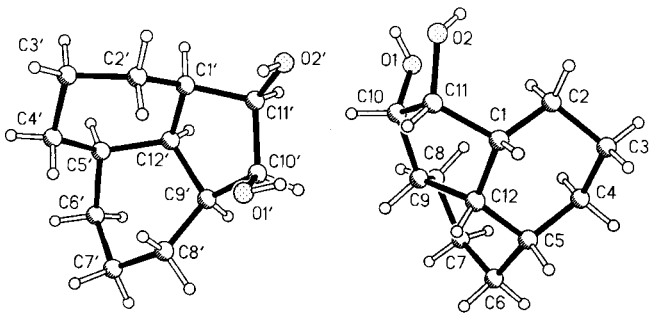


Figure 2. The two independent molecules of compound **14** in the crystal. Radii are arbitrary

b) Isomerization of *cis,trans,trans*-1,5,9-Cyclododecatriene

The isomerization was performed as described earlier[7,8]. The authors claim to have obtained a reaction mixture containing 50% of one ufolane isomer (called DHAN III); none of the other possible isomers could be detected.

We used a ratio of cyclododecatriene to polyphosphoric acid of 3:1. The fraction boiling at 124 °C/2 kPA was investigated by GC/MS. Several peaks of the molecular mass of ufolane (164) could be detected, but only two compounds, with the retention time of no. 3 and 4, showed the typical fragmentation pattern of the ufolanes (loss of C_2H_4 followed by elimination of CH_3). They amount to 13.5 and 13.3% of the reaction mixture.

c) Reduction of Acenaphthene with Hydrogen Iodide

The product mixture obtained by reduction of acenaphthene with hydrogen iodide at 260 °C[3] was also investigated by GC/MS. It contained six compounds with the molecular mass of ufolane (164) and one with the molecular mass 158 (tentatively a hexahydroacenaphthylene). Five of the six compounds with the mass 164 could be identified as ufolanes on the basis of their retention time and fragmentation pattern. Their content in the reaction mixture (no./%: 1/11.7, 2/3.9, 3/33.7, 4/31.5, and 5/19.2), especially the low content of **1** and the high content of **5**, show that the formation of the ufolanes under these conditions is not entirely determined by the relative thermodynamic stabilities of the isomers as calculated by MMX.

Discussion of the X-ray Structures

As in the *c,c,c*-ufolane derivative **13** (ref.[10]), the six-membered rings of **24** (Figure 1) exhibit different conformations;

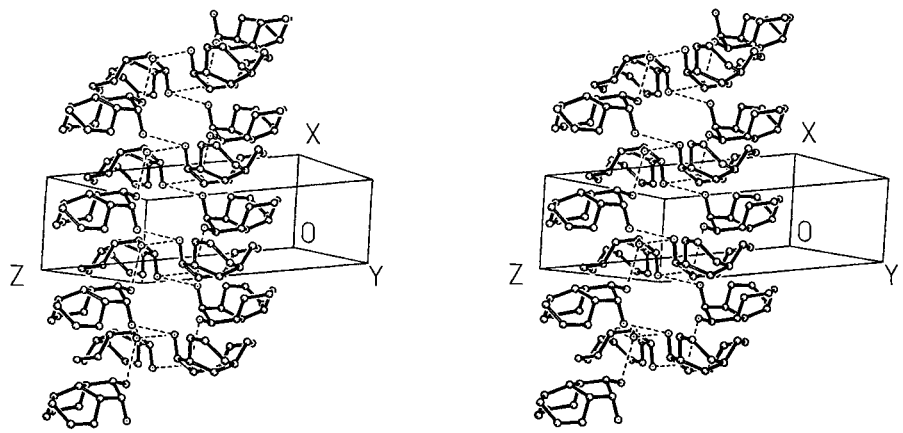


Figure 3. Stereoscopic packing diagram of compound **14**, showing one of two "columns" in the unit cell; the molecules are connected by hydrogen bonds (dashed lines). Hydrogen atoms are omitted for clarity

the ring C1 – 5,C12 is a somewhat flattened chair and the ring C5 – 9,C12 a twist form. The same is true of both independent molecules of **14** (Figure 2). Hydrogen bonding connects the molecules of **14** to form columns with hydrophilic interiors parallel to the *x* axis (Figure 3); the H-bonded distances (donor first; symmetry operators refer to the second atom) are O1′···O1 285 (1 + *x*, *y*, *z*), O1···O2 285 (– *x*, – *y*, 1 – *z*), O2···O2′ 290 (– *x*, – *y*, 1 – *z*), O2′···O2 306 pm (1 – *x*, – *y*, 1 – *z*).

In the *c,c,t*- and *t,t,t*-ufolane derivatives **23** (Figure 4) and **11** (Figure 5) both six-membered rings adopt chair conformations (as does the *t,t,t*-ufolane derivative **21**, see ref.[10]). The five-membered rings are characterized by an envelope conformation with a small torsion angle about the C10 – C11 bond (– 2°); this may be attributed to the effect of the substituents at C10 and/or C11. In **23** the tosyl group (atoms S,C13 – 19) is perpendicular to the plane about the C = N bond (atoms C9 – 11,N1,N2); assuming that the hydrogen position is reliable, a pyramidal geometry is observed for N2, which lies 35 pm out of the plane of its bonding partners.

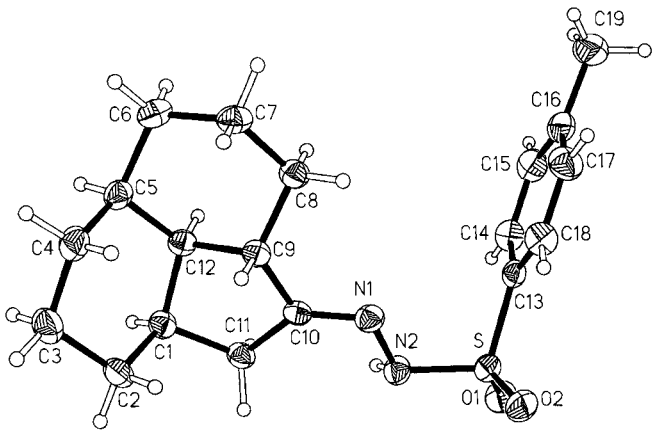


Figure 4. The molecule of compound **23** in the crystal. Thermal ellipsoids correspond to 50% probability. Hydrogen radii are arbitrary

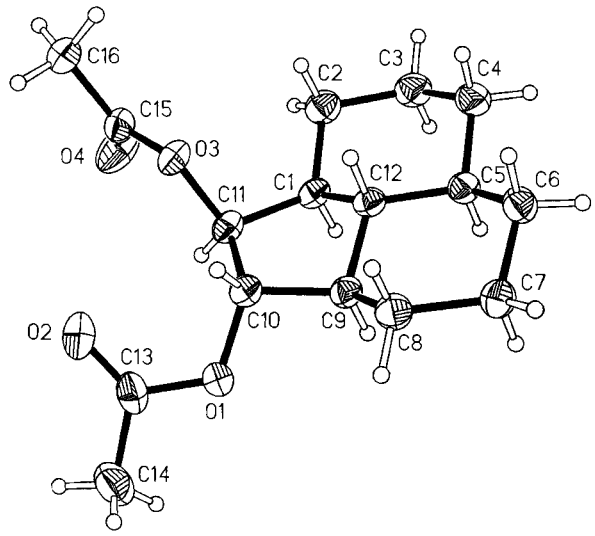


Figure 5. The molecule of compound **11** in the crystal. Thermal ellipsoids correspond to 50% probability. Hydrogen radii are arbitrary

This investigation was supported by the *Fonds der Chemischen Industrie*.

Experimental

NMR: Bruker AM 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Shifts refer to TMS as internal standard. – IR: Nicolet 320 FT-IR or AccuLab 4 (Beckman Instruments). – MS: Finnigan MAT 8430 (70 eV). – GC-MS: Finnigan MAT 4515 (40 eV) and Carlo Erba 5160 chromatograph, 30-m fused silica capillary column DB-1 (diameter 0.32 mm, Carlo Erba). – Gas chromatograms: Carlo Erba 2000 with a 25-m fused silica capillary column FS-SE-30-CB-0.25 (Macherey & Nagel). – Melting points: not corrected. – TLC: SiO_2-coated sheets (Polygram SIL G/UV_{254}, Macherey & Nagel).

cis-1,2-Dihydroxyacenaphthene (**10**): 25.0 g (139 mmol) of **9** was reduced with 11.0 g (291 mmol) of $NaBH_4$ as described earlier[10], but instead of tetrahydrofuran 250 ml of diethyl ether was used. After workup, the crude product was recrystallized from ethanol to afford 6.7 g (37 mmol) of **10** (26%). Evaporation of the mother liquor yielded 5.2 g (28 mmol) of **8** (20%). TLC (dichloromethane/acetone, 4:1): R_f = 0.47 (R_f of the *trans*-diol **8** = 0.26); m.p. 211 °C (ref.[34] 213 °C). – IR (KBr): $\tilde{\nu}$ = 3330 cm^{-1} (OH), (3180) (OH). – ^{1}H NMR ([D_6]DMSO): δ = 5.30 (s, 4H, OH, C*H*OH), 7.49 (d, 2H, *J* = 7 Hz, 3,8-H), 7.57 (dd, 2H, *J* = 8/7 Hz, 4,7-H), 7.77 (d, 2H, *J* = 8 Hz, 5,6-H).

(1α,5α,9α,10β,11α,12α)-Dodecahydro-10,11-acenaphthylenediol (*c,c,c-trans-10,11-Ufolanediol*, **13**): 17.8 g (96 mmol) of **8**[10], dissolved in 400 ml of ethanol and 600 ml of cyclohexane, was stirred with 400 mg of Nishimura catalyst[35] under hydrogen (15 MPa) at 40 °C for 24 h. The mixture was filtered, and the solvents were evaporated. The resulting residue was recrystallized from ethyl acetate to yield 13.5 g (69 mmol) of **13** (72%), m.p. 129 °C, identical with compound **6d** in ref.[10] TLC (dichloromethane/acetone, 4:1): R_f = 0.14. – Reduction (60 h, 0.36 MPa) of 3.0 g (16 mmol) of **8** with 1.5 g of rhodium catalyst (5% rhodium on aluminium oxide) yielded 2.2 g (16 mmol) of **13** (69%).

(1α,5α,9α,10β,11β,12α)-Dodecahydro-10,11-acenaphthylenediol [*(10β,11β)-c,c,c-10,11-Ufolanediol*, **14**]: A suspension of 7.35 g (40 mmol) of **10** in 200 ml of anhydrous ethanol and 450 ml of cyclohexane was stirred with 50 mg of zinc chloride[36] and 300 mg of Nishimura catalyst[35] under hydrogen (18 MPa) at 40 °C for 24 h. The mixture was filtered and the filtrate was concentrated by evaporation of the solvents and then cooled to – 20 °C. The obtained residue yielded after recrystallization from ethanol/pentane 2.9 g (15 mmol, 40%) of **14**, m.p. 118 – 120 °C, identical with compound **6a** in ref.[10] (TLC). – From the mother liquor after further evaporation of the solvent and recrystallization of the residue from ethanol/pentane 1.4 g (7 mmol) a mixture of **14** and an isomeric 10,11-ufolanediol was obtained the latter of which proved to be identical with compound **6c** in ref.[10]

(1α,5α,9α,10β,11α,12α)-Dodecahydro-10,11-acenaphthylenediol Bis(methanesulfonate): To a well stirred solution of 18.1 g (92.3 mmol) of **13**[10] in 80 ml of anhydrous pyridine was added dropwise at – 5 °C 21.42 ml (275 mmol) of methanesulfonyl chloride. After stirring at 0 °C for 4 h the reaction was quenched with 370 ml of water and the mixture acidified with 6 N HCl. After filtration and drying 32.1 g (92 mmol, 99%) of the bis(methanesulfonate), m.p. 122 °C (dichloromethane/ligroine), was obtained. TLC: R_f = 0.49 (ligroine/ethyl acetate 1:1). – IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1}, 2873, 1350

(SO), 1175 (SO). – ^{1}H NMR ([D$_6$]acetone): δ = 1.00–1.10 (m, 1H), 1.15–1.26 (m, 1H), 1.35 (dq, *J* = 12.7/3.6 Hz, 1H), 1.43–1.60 (m, 5H), 1.67–1.76 (m, 1H), 1.78–1.86 (m, 3H), 2.04–2.15 (m, 2H), 2.41 (m, 1H, 1-H or 9-H), 2.51 (m, 1H, 1-H or 9-H), 3.15, 3.19 (2 s, 6H, CH_3), 4.48 (dd, *J* = 7.8/6.2 Hz, 1H, 10-H or 11-H), 5.06 (dd, *J* = 7.8/6.2 Hz, 1H, 10-H or 11-H). – ^{13}C NMR ([D$_6$]acetone): δ = 17.7, 24.0, 24.4, 24.7, 25.5, 30.1 (CH_2), 31.4, 35.6, 38.1 (CH), 38.6, 38.7 (CH_3), 40.4 (CH), 85.8, 90.0 (C-10,11). – MS (70 eV): *m/z* (%) = 256 (3) [M – CH_3SO_3H], 246 (14), 177 (38), 160 (100) [M – 2 CH_3SO_3H]. – MS (70 eV, CI, NH_3): *m/z* (%) = 370 (100) [M + NH_4^+], 177 (1), 161 (8), 160 (8).

$C_{14}H_{24}O_6S_2$ (352.5) Calcd. C 47.71 H 6.86 O 27.24
Found C 47.59 H 6.79 O 27.07

(1α,5α,9α,12α)-1,2,3,4,5,6,7,8,9,12-Decahydroacenaphthylene (c,c,c-10-Ufolene, **19**)

a) *From* **14**: Under dry oxygen-free nitrogen 3.7 ml (33 mmol) of titanium(IV) chloride was distilled into an anhydrous, ice-cooled mixture of 3.1 g (15.8 mmol) of **14**, 90 ml of tetrahydrofuran, 4.5 g (69 mmol) of zinc dust, and 2.5 ml of pyridine. After refluxing for 4 d, the mixture was extracted exhaustively with pentane. The extraction with pentane was repeated after quenching with 10% aqueous potassium carbonate. The united organic phases were washed and dried and then concentrated by evaporation of the solvent, and the unreacted crystallized **14** was filtered off. After further concentration of the filtrate, the residue yielded by bulb-tube distillation 0.20 g (1.23 mmol) of **19** (8%).

b) *From* **13**: To a refluxing mixture of 5.0 g (25.5 mmol) of **13**, 26.8 g (102 mmol) of triphenylphosphane, 7.0 g (102 mmol) of imidazole, a spatula tip of zinc, and 500 ml of toluene was added 15.4 g (60.7 mmol) of iodine in portions over a period of 3 h. After 1 h of continued refluxing, **13** could no longer be detected by TLC in the reaction mixture. After cooling to room temp. 5 g of iodine and 125 ml of 1.4 N NaOH were added. The organic phase was separated, washed with aqueous sodium thiosulfate and sodium hydrogen carbonate and dried with sodium sulfate. After evaporation of the solvent, the residue was dissolved in ligroine, and the solution was filtered through silica gel. Evaporation and distillation of the eluate yielded 900 mg (5.6 mmol) of **19** (22%), b.p. 53°C/80 Pa. Retention index[29,30] $I^{SE\text{-}30}$ (*T* = 130°C): 1236. – IR (film): $\tilde{\nu}$ = 3042 cm^{-1}, 2924, 2861, 742. A C=C band could not be detected, but in the Raman spectrum there was a band at 1612 cm^{-1} (2.5-W laser, slit 30/40/40/30, 24°C, measurement of isotropy/anisotropy). – ^{1}H NMR[38] ($CDCl_3$): δ = 1.09 (m, 2H, 2,8-H), 1.3–1.7 (m, 8H, 3,4,6,7-H), 1.76 (m, 2H, 2,8-H), 1.92 (m, 1H, 5-H), 2.3 (dd, *J* = 6/12 Hz, 1H, 12-H), 2.57 (m, 2H, 1,9-H), 5.72 (d, *J* = 1 Hz, 2H, 10,11-H). – ^{13}C NMR[38] ($CDCl_3$): δ = 20.4 (C-3,7), 27.9 (C-4,6), 28.8 (C-2,8), 31.0 (C-5), 38.3 (C-12), 43.5 (C-1,9), 135.5 (C-10,11). – MS (70 eV): *m/z* (%) = 162 (45) [M$^+$], 147 (4), 134 (44), 133 (46), 119 (61), 105 (28), 91 (100), 79 (56).

$C_{12}H_{18}$ (162.3) Calcd. C 88.82 H 11.18
Found C 88.90 H 11.05

(1α,5α,9α,10β,11α,12α)-10,11-Dibromododecahydroacenaphthylene (trans-10,11-Dibromo-c,c,c-ufolane, **24**): A solution of 1.5 g of bromine in 3 ml of chloroform was added dropwise to an ice-cooled solution of 1.24 g (7.6 mmol) of **19** in 5 ml of chloroform until no more discoloration occurred. After washing the solution with aqueous sodium thiosulfate, drying, evaporation of the solvent at reduced pressure and several recrystallizations of the residue from pentane, 1.1 g (3.4 mmol) of **24** (45%) was obtained as colorless needles; m.p. 84°C. – IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2854. – ^{1}H NMR[38] ($CDCl_3$): δ = 0.82 (m, 1H, 8-H), 1.10–1.28 (m, 2H, 6,7-H), 1.30–1.48 (m, 2H, 2,4-H), 1.50–1.63 (m, 3H, 3,4,6-H), 1.71 (m, 1H, 3-H), 1.79–1.88 (m, 2H, 5,7-H), 1.89–1.99 (m, 2H, 2,8-H), 2.18 (m, 1H, 9-H), 2.24–2.43 (m, 2H, 1,12-H), 3.94 (dd, *J* = 7.0/10.3 Hz, 1H, 11-H), 4.33 (dd, *J* = 6.4/10.3 Hz, 1H, 10-H). – ^{13}C NMR[38] ($CDCl_3$): δ = 17.1 (C-3), 24.0 (C-7), 24.8 (C-2), 24.9 (C-4), 26.4 (C-8), 29.7 (C-6), 31.5 (C-5), 38.1 (C-12), 43.4 (C-9), 45.2 (C-1), 61.1 (C-10), 62.1 (C-11). – MS (70 eV): *m/z* (%) = 324, 322, 320 (0.09, 0.3, 0.12) [M$^+$], 243, 241 (8, 8), 161 (100), 133 (8).

$C_{12}H_{18}Br_2$ (322.1) Calcd. C 44.75 H 5.63
Found C 44.63 H 5.61

(1α,5α,9α,12α)-Dodecahydroacenaphthylene (c,c,c-Ufolane, **5**): A solution of 1.80 g (11.1 mmol) of **19** in 100 ml of cyclohexane was hydrogenated [3 g of rhodium (5%)/aluminium oxide, 0.3 MPa] at 25°C. The reaction mixture was filtered and the solvent evaporated from the filtrate. Distillation of the residue yielded 1.16 g (7.06 mmol) of **5** (64%), b.p. 61°C/0.7 hPa, m.p. 4–6°C (ref.[6] 10.8–11.5°C). d^{23} = 0.96 ± 0.01 g/mol (ref.[6] d^{22} = 0.954 g/mol). n_D^{20} = 1.5021 (ref.[6] 1.5024). – IR (film): $\tilde{\nu}$ = 2920 cm^{-1}, 2850, 1460, 1440. – ^{1}H NMR ($CDCl_3$): δ = 1.0–2.0 (m). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 31.6 (CH_2), 31.9 (CH), 38.0 (CH), 40.9 (CH). – ^{13}C NMR[11]: δ = 21.4 (C-3,7), 28.6 (C-10,11), 28.8 (C-2,8), 31.8 (C-4,6), 32.2 (C-5), 38.3 (C-1,9), 41.2 (C-12). – MS (70 eV): *m/z* (%) = 164 (50) [M$^+$], 136 (40), 135 (31), 121 (100), 107 (15).

$C_{12}H_{20}$ (164.3) Calcd. C 87.73 H 12.27
Found C 87.85 H 12.19

Catalytic Hydrogenation of (1α,5α)-1,2,3,4,5,6,7,8,10,11-Decahydro-10-acenaphthylenone (**12**): 9.0 g (51 mmol) of **12**[10] in 80 ml of dry hexane was shaken for 2 h over 2.5 g of palladium (5%)/active carbon under hydrogen (35 MPa) at 20°C. The mixture was filtered and the solvent evaporated from the filtrate. Distillation of the residue yielded fraction 1, b.p. 97°C/0.7 kPa: 0.89 g (5.5 mmol, 11%); fraction 2, b.p. 121°C/0.7 kPa: 6.5 g (36 mmol, 71%).

Fraction 1: 2,3,4,5,6,7,8,9,10,11-Decahydroacenaphthylene [1(12)-Ufolene, **25**]: ^{1}H NMR ($CDCl_3$): δ = 0.80–2.50 (m). – ^{13}C NMR ($CDCl_3$): δ = 22.9, 25.7, 25.8, 30.3, 30.9, 34.2, 34.8 (CH_2), 35.3 (CH), 35.6 (CH_2), 44.8 (CH), 132.2, 140.0 (C-1,12). – MS (70 eV): *m/z* (%) = 162 (100) [M$^+$], 147 (8), 134 (84), 133 (50), 119 (60), 105 (28), 91 (68), 79 (32).

Fraction 2 is a 1:1 mixture of two ufolanones (GC/MS). After refluxing of 7.9 g (44 mmol) of fraction 2 for 1 h in 40 ml of methanol/5 ml of 2 N HCl and evaporation of the major part the methanol at reduced pressure, water was added and the mixture extracted several times with ether. The combined ether layers were washed, dried, and concentrated. On distillation the residue yielded 6.0 g (34 mmol) of *(1α,5α,9β,12α)-dodecahydro-10-acenaphthyleneone (c,c,t-10-ufolanone,* **18**) (77%), b.p. 135°C/1.1 kPa. – IR (film): $\tilde{\nu}$ = 2925, 2860 cm^{-1} (C–H), 1740 (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.01–2.30 (m). – ^{13}C NMR ($CDCl_3$): δ = 21.5, 24.1, 25.4, 25.5, 27.9, 30.9 (C-3,4,6,7,8), 31.6, 34.8, 44.4, 45.0 (C-1,5,9,12), 44.2 (C-11), 218.6 (C-10). – MS (70 eV): *m/z* (%) = 178 (100), 160 (18), 149 (23), 136 (74), 134 (41).

$C_{12}H_{18}O$ (178.3) Calcd. C 80.85 H 10.18 O 8.97
Found C 80.96 H 10.11 O 8.93

(1α,5α,9β,12α)-Dodecahydro-10-acenaphthylenone (c,c,t-10-Ufolanone, **18**) *from 1-Hydroxyacenaphthene:* 30.0 g (176 mmol) of 1-hydroxyacenaphthene was shaken in 700 ml of cyclohexane and 50 ml of anhydrous ethanol at 45°C for 5 d with 0.5 g of lithium chloride and 1.9 g of Nishimura catalyst[35] under hydrogen (20 MPa). To a solution of the viscous oil (29 g), obtained by filtration and evaporation of the solvent of the filtrate, in pure acetone was added dropwise a solution of 25 g of chromium trioxide in 65 ml of water and 21 ml of conc. sulfuric acid together with oc-

casional small portions of anhydrous magnesium sulfate[19,37]. When the orange color persisted for about 10 min, stirring was continued for 3 min and solid sodium hydrogen carbonate was added. The filtrate of the reaction mixture gave after concentration and distillation (b.p. 74°C/1 Pa) 14.36 g (80 mmol, 46%) of **18**.

(1α,5α,9β,12α)-Dodecahydro-10-acenaphthylenone Tosylhydrazone (c,c,t-10-Ufolanone Tosylhydrazone, **23**): 9.0 g (50 mmol) of **18** or a mixture of the ketones **17** and **18** was added dropwise at 60°C to 13.0 g (70 mmol) of tosylhydrazine in 10 ml of 2 N HCl. The crystalline precipitate was separated and recrystalled from methanol to yield 14.3 g (41 mmol) of **23** (82%), m.p. 157°C. – IR (KBr): $\tilde{\nu}$ = 3226 cm^{-1} (N–H); 2961, 2925, 2878, 2860, 2845 (C–H). – ^1H NMR ($CDCl_3$): δ = 0.95–2.39 (m, 18H, CH), 2.42 (s, 3H, CH_3), 7.27 (s, 1H, NH), 7.30, 7.84 (AA'XX' spectrum, Ar-H). – ^{13}C NMR ($CDCl_3$): δ = 21.6 (CH_3), 21.3, 24.4, 25.5, 27.5, 27.8, 30.9, 34.2 (C-2,3,4,6,7,8,11), 34.5, 34.9, 40.3, 46.4 (C-1,5,9,12), 128.1 (C-3',5'), 129.4 (C-2',6'), 135.5 (C-4'), 143.8 (C-1'), 168.0 (C-10). – MS (70 eV): *m/z* (%) = 346 (5) [M^+], 191 (100), 161 (32).

$C_{19}H_{26}N_2O_2S$ (346.5)
Calcd. C 65.86 H 7.56 N 8.09 O 9.23 S 9.25
Found C 65.92 H 7.63 N 8.17 O 9.20 S 9.38

(1α,5α,9β,12α)-Dodecahydroacenaphthylene (c,c,t-Ufolane, **3**): 40.0 g (1.06 mol) of $NaBH_4$ was added in portions to a refluxing solution of 18 g (52 mmol) of **23** in 600 ml of methanol. After the end of the nitrogen evolution the reaction mixture was refluxed for 10 h and then treated with water. The mixture was extracted with petroleum ether. After neutralization of the aqueous layer with HCl, its extraction with ether and concentration of the combined dried ethereal phases 13.4 g (39 mmol) of the unreacted hydrazone **23** was obtained. After washing with water and drying, the petroleum ether layers were concentrated. On distillation the residue yielded 1.8 g (11 mmol) of **3** (21%, 82% with respect to converted **23**), b.p. 99°C/1.1 kPa. d^{20} = 0.93 ± 0.01 g/ml. – IR (film): $\tilde{\nu}$ = 2921, 2892, 2858, 1446 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.83–2.04 (m). – ^{13}C NMR ($CDCl_3$): δ = 22.3, 26.1, 26.5, 29.3, 30.4, 30.7, 31.6, 32.5 (C-2,3,4,6,7,8,10,11), 34.8, 35.5, 37.5, 48.6 (C-1,5,9,12). – ^{13}C NMR[11]: δ = 22.6 (C-7), 26.4 (C-2), 26.5 (C-4), 26.8 (C-3), 29.6 (C-11), 30.7 (C-10), 31.1 (C-8), 32.9 (C-6), 35.2 (C-1), 35.9 (C-9), 37.3 (C-5), 49.0 (C-12). – MS (70 eV): *m/z* (%) = 164 (32) [M^+], 136 (30), 121 (100), 107 (15), 93 (33), 79 (50).

$C_{12}H_{20}$ (164.3) Calcd. C 87.72 H 12.27
Found C 87.58 H 12.20

1,2,3,4,5,6,7,8,10,11-Decahydro-11-hydroxy-10-acenaphthylenone (11-Hydroxy-9(12)-ufolen-10-one, **28**) *and 1,2,3,4,6,7,8,9,10,11-Decahydro-10,11-acenaphthylenediol [5(12)-Ufolene-10,11-diol,* **29**]: 200 ml of ammonia and 10.5 g (0.456 mol) of sodium were added to 200 ml of cooled (–50°C) anhydrous ether. To this mixture was added dropwise with stirring over a period of 2 h without further external cooling a solution of 29.0 g (0.115 mmol) of 1,8-bis(ethoxycarbonyl)-$\Delta^{9,10}$-octaline (**26**) in anhydrous ether. Some pieces of undissolved sodium could, however, still be seen in the decolorized solution, and therefore another 100 ml of liquid ammonia was added. After stirring for 2 h, 100 g of ammonium chloride and 100 ml of water were added, and after evaporation of the ammonia another 200 ml of water was added. The acidified (6 N HCl) solution was extracted several times with ether. The united extracts were washed, dried, and concentrated. The residue was chromatographed on silica gel with ethyl acetate/dichloromethane (1:1) with **27**, if present, eluting first (R_f = 0.8, TLC, ethyl acetate/dichloromethane, 1:1). The fraction containing a colorless compound with R_f = 0.5 (TLC, ethyl acetate/dichloromethane, 1:1) yielded 14.32 g (74.6 mmol) of **28** (65%) after evaporation of the solvents; m.p. 105–108°C. – ^1H NMR[38] ([D_6]DMSO): δ = 0.91–1.17 (m, 3H, 2,4,6-H), 1.29–1.48 (m, 2H, 3,7-H), 1.69–1.82 (m, 2H, 3,7-H), 1.82–1.98 (m, 3H, 4,6,8-H), 2.03–2.13 (m, 1H, 8-H), 2.13–2.23 (m, 1H, 2-H), 2.26–2.38 (m, 2H, 1,5-H), 3.62–3.64 (ddd, $^3J_{CH-OH}$ = 6, $^3J_{CH-CH}$ = 2.8, ^4J = 1 Hz, 1H, 11-H), 5.50 (d, *J* = 6 Hz, 1H, OH). – ^{13}C NMR[38] ([D_6]DMSO): δ = 206.0 (C-10), 173.8 (C-12), 133.1 (C-9), 78.6 (C-11), 47.1 (C-1), 35.9 (C-5), 32.6 (C-4), 31.1 (C-2), 29.5 (C-6), 23.6 (C-3), 21.0 (C-7), 19.6 (C-8). – MS (70 eV): *m/z* (%) = 192 (100) [M^+], 175 (15), 164 (11), 163 (30).

$C_{12}H_{16}O_2$ (192.1) Calcd. C 74.95 H 8.39 O 16.65
Found C 75.11 H 8.19 O 16.70

The fraction containing a compound with R_f = 0.25 (TLC, ethyl acetate/dichloromethane, 1:1) yielded 0.15 g (0.75 mmol) of **29** (6.5%) after evaporation of the solvents; m.p. 167–170°C. – ^1H NMR ([D_6]DMSO): δ = 1.07 (m, 1H), 3.23, 3.31 (m, 1H), 1.76–1.90 (m, 5H), 3.23–3.31 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 133.3, 124.1 (C-5,12), 80.5 (C-10,11), 43.6 (C-1,9), 27.0, 25.4, 22.7 (C-2,8, C-3,7, C-4,6). – MS (70 eV): *m/z* (%) of = 194 (38) [M^+], 176 (52), 148 (50), 147 (48), 135 (86), 91 (100).

$C_{12}H_{18}O_2$ (194.1) Calcd. C 74.19 H 9.34 O 16.47
Found C 74.10 H 9.25 O 16.65

The described preparation of **28** could not be reproduced in every case. One experiment with 30.4 g of **26** and only 3.4 g of sodium yielded 8.2 g (35%) of **27**[10] exclusively.

Dodecahydro-11-hydroxy-10-acenaphthylenone (11-Hydroxy-10-ufolanone, **30**): A suspension of 266.8 g (468 mmol) of Ag_2CO_3 on Celite[39] in 1.2 l of benzene was refluxed with 10.0 g (51 mmol) of **13** until no more **13** was detectable (GC, 3 h). After concentration the filtrate yielded on distillation 7.0 g (36 mmol) of **30** (71%), b.p. 95°C/10 Pa. – IR (film): $\tilde{\nu}$ = 3410 cm^{-1} (OH), 1710 (CO). – MS (70 eV): *m/z* (%) = 194 (100) [M^+], 176 (41), 148 (89).

Oxidation of 11-Hydroxy-10-ufolanone (**30**): A solution of 1.5 g (15.0 mmol) of chromium trioxide in 34 ml of acetic acid and 8 ml of water was added dropwise at 20°C to a solution of 1.0 g (5.2 mmol) of **30** in 10 ml of acetic acid. The progress of the reaction was monitored by GC (SE-30 capillary column, 200°C). After 24 h no further conversion could be detected. After the addition of water the reaction mixture was extracted several times with dichloromethane. The combined extracts were washed and dried. After evaporation of the solvent the residue was crystallized from ethanol to furnish 0.30 g (1.3 mmol) of *decahydro-1,8-naphthalenedicarboxylic acid*, m.p. 209°C (ref.[40] 213°C). – IR (KBr): 2940 cm^{-1} (OH), 2920 (OH), 2830 (OH), 1700 (C=O). – MS (70 eV): *m/z* (%) = 208 (100) [M^+], 190 (23), 180 (68), 135 (67).

(1α,5α)-1,2,3,4,5,6,7,8,10,11-Decahydro-10-acenaphthylenone [c,c-9(12)-Ufolen-10-one, **12**] *from the Ketols* **27** *and* **28**: To a solution of the ketols in acetic acid was added hydroiodic acid and, after refluxing for 1 h, the threefold volume of cold 2 N NaOH. Free iodine was reduced by addition of aqueous sodium sulfite. The reaction mixture was extracted several times with ether. The combined extracts were washed with aqueous sodium sulfite, 2 N NaOH, and water and dried. After evaporation of the solvent the residue was distilled. Reduction of pure **27** [0.8 g (4.1 mmol), 13 ml acetic acid, 2.2 ml hydroiodic acid (57%)] yielded 0.53 g (3.0 mmol) of **12** (73%); reduction of pure **28** [2.9 g (15 mmol), 45 ml acetic acid, 8.2 ml hydroiodic acid (57%)] yielded 1.77 g (10 mmol) of **12** (67%, the spectra were identical with those described in ref.[10] for **12**).

12 *and (1α,5α,12α)-1,2,3,4,5,6,7,10,11,12-Decahydro-10-acenaphthylenone (c,c-8-Ufolen-10-one,* **32**) *or [c,c-1(11)-Ufolen-10-one,* **33**] *from* **13**: A mixture of 25.0 g (127.6 mmol) of **13**, 4.2 g (4.4 mmol)

of tris(triphenylphosphane)ruthenium dichloride, and 100 ml of triethyleneglycol dimethyl ether was heated under nitrogen to 200°C. The progress of the reaction was monitored by GC (SE-30 capillary column, 200°C). After 3 h all **13** had reacted. The mixture was heated for a further 30 min and filtered after the addition of 250 ml of water and 200 ml of ether. The aqueous phase was extracted several times with ether. After concentration of the combined ethereal phases, the residue yielded on distillation 16.5 g (93 mmol) of **12/32** or **33** (10:1, GC, SE-30 capillary column, 200°C), b.p. 66–76°C/0.8 Pa (pure **12** b.p. 74°C/0.8 Pa, ref.[10]). GC (DB 1-30W-column, carrier helium, t_1 = 150°C, R = 6°/min, t_2 = 300°C)/MS (70 eV), **12**: m/z (%) = 176 (92) [M^+], 148 (51), 134 (100). – **32** or **33**: m/z (%) = 176 (8) [M^+], 148 (2), 134 (100).

(1α,5α,9α,12β)-Dodecahydro-10-acenaphthylenone (t,t,t-10-Ufolane, **16***) and (1α,5α,9β,12α)-Dodecahydro-10-acenaphthylenone (c,c,t-10-Ufolanone,* **18**): 10.0 g (57 mmol) of **12** containing 10% of **32** or **33** was reduced with lithium in liquid ammonia/ether as described earlier for pure **12**[10]. Workup by distillation (b.p. 41–54°C/10^{-2} Pa, ref.[10] 44°C/0.4 Pa) yielded 5.4 g (30 mmol) of **16/18** (5:1, GC, SE-30 capillary column, 200°C). Fractional distillation gave pure **16**, b.p. 44°C/0.1 Pa.

(1α,5α,9α,12β)-Dodecahydro-10-acenaphthylenone Tosylhydrazone (t,t,t-10-Ufolanone Tosylhydrazone, **21**): 4.8 g (27 mmol) of **16/18** (5:1) was added to a solution of 5.4 g (29 mmol) of tosylhydrazine in 50 ml of methanol and 1.6 ml of 2 N HCl at 50°C. The mixture of **21** and **23** (6.6 g, 19 mmol, 71%) crystallized on cooling to 20°C. Pure **21** (5.5 g, 16 mmol, 59%) could be obtained by recrystallization from methanol, m.p. 168°C (168°C, ref.[10]).

(1α,5α,9α,12β)-Dodecahydroacenaphthylene (t,t,t-Ufolane, **1**): 29.0 g (763 mmol) of $NaBH_4$ was added in small portions to a well stirred and ice-cooled solution of 14.4 g (42 mmol) of **21** in 700 ml

Table 2. Crystal data and details of refinement for compounds **24**, **14**, **23**, and **11**

Compound	**24**	**14**	**23**	**11**
Formula	$C_{12}H_{18}Br_2$	$C_{12}H_{20}O_2$	$C_{19}H_{26}N_2O_2S$	$C_{16}H_{24}O_4$
M_r	322.1	196.3	346.5	280.4
Crystal habit	Colourless needle	Colourless prism	Colourless prism	Colourless square tablet
Crystal size (mm)	0.7 x 0.15 x 0.15	0.8 x 0.6 x 0.3	0.9 x 0.3 x 0.25	0.4 x 0.4 x 0.15
Space group	$P2_1/n$	P1	$P2_1/n$	$P2_1/c$
Cell constants :				
a (pm)	909.9(4)	544.5(3)	1449.8(4)	950.9(3)
b (pm)	1338.8(6)	1447.8(6)	5.1692(15)	2089.9(7)
c (pm)	975.0(4)	1476.4(7)	2378.6(6)	758.9(3)
α (°)		113.62(3)		
β (°)	92.34(3)	98.72(4)	91.31(2)	98.92(2)
γ (°)		93.50(3)		
V (nm^3)	1.1868	1.0444	1.7821	1.4899
Z	4	4	4	4
D_x ($Mg\ m^{-3}$)	1.80	1.25	1.29	1.25
$F(000)$	640	432	744	608
μ (mm^{-1})	6.7	0.07	0.18	0.08
No. of reflections :				
measured	2757	3828	6998	5660
independent	2079	3671	3129	2619
R_{int}	0.018	0.016	0.019	0.020
observed [$>4\ \sigma(F)$]	1498	3030	2467	1834
R	0.031	0.040	0.035	0.039
wR	0.032	0.049	0.042	0.043
g	0.0003	0.0002	0.0003	0.0003
No. of parameters	127	269	221	185
S	1.1	2.2	1.6	1.5
Max. Δ/σ	0.001	0.002	0.001	0.003
Max. $\Delta\rho$ ($e\ pm^{-3}\ x10^6$)	0.4	0.4	0.2	0.1

of methanol. After the vigorous evolution of nitrogen had ceased, the mixture was refluxed for 15 h. Then 200 ml of water and 200 ml of petroleum ether were added. From the aqueous phase unreacted **21** (6.7 g, 19 mmol) crystallized. The organic phase was separated and yielded 1.6 g (10 mmol) of **1** (43%) after washing, drying, concentration, and distillation, b.p. 53°C/40 Pa. $d^{20} = 0.91 \pm 0.01$ g/ml. – ^{1}H NMR ($CDCl_3$): δ = 0.07–1.90 (m). – ^{13}C NMR ($CDCl_3$): δ = 26.8, 29.4, 32.4, 32.8 (CH_2), 40.9, 43.2, 57.9 (CH_2). – ^{13}C NMR ($CDCl_3$), ref.[11]: δ = 26.9 (C-3,7), 29.4 (C-10,11), 32.5 (C-2,8), 33.0 (C-4,6), 41.1 (C-5), 43.4 (C-1,9), 57.9 (C-12). – MS (70 eV): *m/z* (%) = 164 (75) [M^+], 136 (71), 121 (100), 107 (20), 94 (26), 79 (38), 67 (37).

$C_{12}H_{20}$ (164.3) Calcd. C 87.73 H 12.27
Found C 87.78 H 12.23

(1α,5α,9α,10β,11α,12α)-10,11-Diacetoxydodecahydroacenaphthylene (trans-10,11-Diacetoxy-c,c,c-ufolane, **7**): A solution of 9.8 g (50 mmol) of **13** in 15 ml of acetic anhydride and 5 ml of dry pyridine was refluxed for 4 h, then poured on 100 ml of ice and acidified with 10% hydrochloric acid. The precipitate was coolected by filtration. After washing and drying 9.7 g (34.6 mmol) of **7** (69%) resulted, m.p. 66°C (ethyl acetate). – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 1730 (CO), 1240. – ^{1}H NMR ($CDCl_3$): δ = 0.96–1.92 (m, 14H), 2.04 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.36 (m, 2H, 1,9-H), 5.13 (m, 2H, C*H*OAc). – ^{13}C NMR: δ = 21.0, 21.2 (2 CH_3), 17.5, 23.3, 23.8, 25.2, 25.4, 29.4 (C-2,3,4,6,7,8), 30.7, 35.9, 39.2, 39.3 (C-1,5,9,12), 79.7, 82.7 (C-10,11), 170.9, 171.0 (2 CO). – MS (70 eV): *m/z* (%) = 280 (1) [M^+], 220 (11), 178 (56), 160 (100).

$C_{16}H_{24}O_4$ (280.4) Calcd. C 68.57 H 8.57 O 22.86
Found C 68.49 H 8.59 O 22.92

(1α,5α,9α,10β,11α,12β)-10,11-Diacetoxydodecahydroacenaphthylene (trans-10,11-Diacetoxy-t,t,t-ufolane, **11**): 3.0 g (10.7 mmol) of **7** and a spatula tip of mercuric bromide in 350 ml of cyclohexane were irradiated at 60°C in an quartz immersion-well apparatus with a low-pressure mercury arc lamp (9 W, TNN 15/32, Hanau Lampengesellchaft). The reaction mixture was stirred by means of oxygen-free nitrogen. The scales on the immersion well were removed from time to time. After 17 h the composition of the reaction mixture no longer changed as shown by GC analysis (fused silica capillary column, 100–300°C, 6°C/min). The composition of the reaction mixture was [peak no./GC retention time [s]/*m/z* (%)]: 1 (14.8%)/722/220 (10), 178 (47), 160 (100); 2 (62.2%, **11**)/733/220 (5), 178 (100), 160 (40); 3 (5.0%)/754/220 (5), 178 (100), 160 (83); 4 (8.2%, **7**)/806/220 (7), 178 (59), 160 (100); 5 (7.2%)/821/220 (3), 178 (100), 160 (48). The reaction mixture was filtered and the filtrate concentrated. The residue was recrystallized from ethyl acetate until the m.p. remained constant; yield 1.6 g (5.7 mmol) of **11** (53%), m.p. 81°C. – IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1}, 1735 (CO), 1242. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (m, 1H), 0.85 (m, 2H), 1.03–1.40 (m, 6H), 1.53 (m, 1H), 1.67 (m, 3H), 1.79 (m, 2H), 1.96 (m, 1H), 2.05 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 4.77 (dd, ^3J = 8.4/1.9 Hz, 1H, C*H*OAc), 5.14 (dd, ^3J = 6.8/1.9 Hz, 1H, C*H*OAc). – ^{13}C NMR: δ = 20.9, 21.08 (CH_3), 25.4, 25.9, 26.2, 29.8, 32.07, 32.08 (C-2,3,4,6,7,8), 41.2, 45.5, 48.4, 51.2 (C-1,5,9,12), 80.9, 85.3 (C-10,11), 170.3, 170.6 (CO). – MS (70 eV): *m/z* (%) = 280 (0.5) [M^+], 220 (17), 178 (100), 160 (39).

$C_{16}H_{24}O_4$ (280.4) Calcd. C 68.57 H 8.57 O 22.86
Found C 68.64 H 8.52 O 22.78

(1α,5α,9α,10β,11α,12β)-Dodecahydro-10,11-acenaphthylenediol (t,t,t-trans-10,11-Ufolanediol, **15**): A solution of 2.6 g (9.2 mmol) of **11** in 90 ml of ethanol and 40 ml of 1 N NaOH was refluxed for 1 h. After cooling to 20°C, the mixture was acidified with 80 ml of 1 N HCl. The precipitate was collected by filtration and recrystallized from ethanol to give 1.7 g (8.7 mmol) of **15** (95%), m.p. 167°C. TLC: R_f 0.13 (SiO_2, dichloromethane/acetone, 80:20). – IR (KBr): $\tilde{\nu}$ = 3326 cm^{-1} (OH), 2925, 2851). – ^{1}H NMR ([D_6]DMSO): δ = 0.56 (m, 1H), 0.75–1.74 (m, 15H), 3.33 (t, *J* = 5 Hz, 1H, C*H*OH), 3.70 (t, *J* = 5 Hz, 1H, C*H*OH), 4.34 (d, *J* = 5 Hz, 1H, OH), 4.69 (d, *J* = 5 Hz, 1H, OH). – ^{13}C NMR: δ = 24.4, 25.2, 25.5, 29.1, 31.36, 31.40 (C-2,3,4,6,7,8), 40.2, 45.2, 49.6, 49.8 (C-1,5,9,12), 79.6, 86.4 (C-10,11). – MS (70 eV): *m/z* (%) = 196 (100) [M^+], 178 (41), 160 (10).

$C_{12}H_{20}O_2$ (196.3) Calcd. C 73.43 H 10.27
Found C 72.44 H 10.07

X-Ray Structure Determinations: Intensity measurements were performed at –95°C on a Siemens R3 diffractometer fitted with an LT-2 low-temperature device. Data were taken to $2\Theta_{max}$ 50°

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (pm^2) for compound **24**

	x	y	z	U(eq)
Br(1)	2817.4(5)	4139.7(3)	4336.2(5)	344(2)
Br(2)	1857.0(6)	5968.5(4)	1577.7(4)	425(2)
C(1)	2846(5)	6058(3)	5831(4)	258(13)
C(2)	1515(5)	5710(3)	6603(4)	309(14)
C(3)	1226(5)	6387(3)	7809(4)	350(15)
C(4)	864(5)	7437(3)	7300(4)	325(14)
C(5)	2128(5)	7888(3)	6516(4)	292(14)
C(6)	1742(5)	8878(3)	5826(5)	334(15)
C(7)	596(5)	8805(3)	4620(4)	277(13)
C(8)	485(5)	7766(3)	3983(4)	265(13)
C(9)	1959(5)	7231(3)	4001(4)	236(13)
C(10)	1800(5)	6133(3)	3561(4)	262(13)
C(11)	2972(5)	5598(3)	4391(4)	274(14)
C(12)	2763(5)	7187(3)	5451(4)	236(12)

Table 4. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (pm^2) for compound **14**

	x	y	z	U(eq)
C(1)	2616(3)	1504(1)	7785(1)	234(6)
C(2)	261(3)	1170(1)	8077(1)	285(6)
C(3)	247(3)	1811(1)	9188(1)	327(7)
C(4)	217(3)	2924(1)	9385(1)	276(6)
C(5)	2447(3)	3354(1)	9088(1)	232(6)
C(6)	2189(3)	4394(1)	9078(1)	257(6)
C(7)	-24(3)	4365(1)	8282(1)	259(6)
C(8)	-611(3)	3356(1)	7330(1)	284(6)
C(9)	1675(3)	2809(1)	7135(1)	246(6)
C(10)	1152(3)	1743(1)	6247(1)	224(6)
C(11)	2607(3)	1066(1)	6652(1)	234(6)
C(12)	3027(3)	2649(1)	8059(1)	217(6)
O(1)	-1481(2)	1371(1)	5938(1)	256(5)
O(2)	1726(2)	3(1)	6103(1)	266(5)
C(1')	3063(3)	1697(1)	2733(1)	276(6)
C(2')	5207(3)	1177(1)	2269(1)	343(7)
C(3')	5463(4)	1353(2)	1334(1)	427(8)
C(4')	6077(3)	2477(2)	1603(1)	382(8)
C(5')	4129(3)	3109(1)	2120(1)	326(7)
C(6')	4990(3)	4251(2)	2588(2)	399(9)
C(7')	7270(3)	4585(1)	3461(1)	359(8)
C(8')	7381(3)	3910(1)	4043(1)	288(7)
C(9')	4797(3)	3427(1)	4022(1)	242(6)
C(10')	4842(3)	2671(1)	4523(1)	232(6)
C(11')	2933(3)	1753(1)	3786(1)	257(6)
C(12')	3248(3)	2825(1)	2932(1)	254(7)
O(1')	7287(2)	2388(1)	4659(1)	269(5)
O(2')	3257(2)	843(1)	3922(1)	298(5)

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (pm^2) for compound **23**

	x	y	z	U(eq)
C(1)	3377(1)	-984(4)	5863.0(7)	253(6)
C(2)	3605(1)	405(4)	6419.0(7)	312(6)
C(3)	2938(1)	-358(5)	6877.8(8)	369(7)
C(4)	1934(1)	219(4)	6711.9(7)	321(6)
C(5)	1653(1)	-1235(4)	6172.8(7)	262(6)
C(6)	678(1)	-633(4)	5936.1(8)	302(6)
C(7)	591(1)	2017(4)	5650.4(8)	304(6)
C(8)	1311(1)	2436(4)	5198.6(8)	278(6)
C(9)	2260(1)	1979(4)	5464.8(7)	233(6)
C(10)	3114(1)	2141(3)	5118.3(7)	233(6)
C(11)	3826(1)	248(4)	5348.9(7)	256(6)
C(12)	2344(1)	-753(3)	5711.0(7)	228(5)
C(13)	2822(1)	4945(3)	3515.2(7)	241(6)
C(14)	2649(1)	2901(4)	3152.4(8)	315(6)
C(15)	1782(1)	2684(4)	2896.8(8)	363(7)
C(16)	1092(1)	4473(4)	2994.3(7)	331(6)
C(17)	1283(1)	6454(4)	3368.5(8)	372(7)
C(18)	2137(1)	6719(4)	3631.5(8)	318(6)
C(19)	170(1)	4314(5)	2693.0(9)	505(8)
N(1)	3150(1)	3662(3)	4698.4(6)	261(5)
N(2)	3981(1)	3469(3)	4388.2(6)	269(5)
S	3929.3(3)	5322.8(9)	3824.2(2)	263(2)
O(1)	4611.4(9)	4322(3)	3458.8(5)	355(5)
O(2)	3993.4(9)	7954(3)	4009.0(5)	337(5)

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (pm^2) for compound **11**

	x	y	z	U(eq)
C(1)	895(2)	6236(1)	2930(2)	260(6)
C(2)	192(2)	5684(1)	1817(3)	334(7)
C(3)	-1429(2)	5708(1)	1829(3)	366(7)
C(4)	-1853(2)	5732(1)	3701(3)	336(7)
C(5)	-1100(2)	6273(1)	4829(2)	270(6)
C(6)	-1321(2)	6288(1)	6781(3)	309(6)
C(7)	-388(2)	6795(1)	7861(3)	317(7)
C(8)	1205(2)	6724(1)	7743(3)	311(6)
C(9)	1383(2)	6736(1)	5792(2)	250(6)
C(10)	2833(2)	6615(1)	5225(2)	267(6)
C(11)	2528(2)	6303(1)	3341(2)	271(6)
C(12)	480(2)	6221(1)	4773(2)	244(6)
C(13)	4914(2)	7218(1)	4880(3)	340(7)
C(14)	5540(2)	7872(1)	4938(3)	479(8)
C(15)	3729(2)	5453(1)	2080(3)	315(7)
C(16)	4429(2)	4820(1)	2451(3)	362(7)
O(1)	3569(1)	7226.1(6)	5252(2)	304(4)
O(2)	5496(2)	6732.3(8)	4544(2)	492(6)
O(3)	3201(1)	5675.5(6)	3509(2)	299(4)
O(4)	3631(2)	5739.1(7)	691(2)	518(6)

with monochromated Mo-K_α radiation. Cell constants were refined from setting angles of ca. 50 reflections in the 2Θ range $20-23°$. For compound **24**, an absorption correction based on ψ scans was applied, with transmission factors 0.68–0.93. Calculations were performed with the program system Siemens SHELXTL PLUS. The structures were solved by heavy-atom (**24**) or direct methods and subjected to anisotropic full-matrix least-squares refinement on F. Hydrogen atoms were included using a riding model. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. For compound **23**, an extinction correction of the form $F_{corr} = F/[1 + 0.002xF^2/\sin 2\Theta]^{0.25}$ was applied; x refined to 0.0011(2). Complete crystal data are given in Table 2, atomic coordinates in Tables 3–6. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55965, the names of the authors, and the journal citation.

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