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# Synthesis of Hexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$.$0^{9,12}$]dodecane-5,11-dione and its Conversion to Di-, Tri-, and Tetranitro-1,3-bishomopentaprismanes

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Sulfenylation of the dianion of dimethyl tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dicarboxylate (**9**) with dimethyl disulfide delivered the *exo,exo*-bis(methylthio) derivative **10a**. Subsequcnt saponification and oxidative decarboxylation resulted in transformation to tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dione (**4**). Upon photolysis of the bisketal **11** of this pivotal intermediate, arrival at the doubly functionalized 1,3-bishomopentaprismane **12** was achieved. Following acidic hydrolysis to give the title compound **5**, elaboration of three dinitro (**14**–**16**), two trinitro (**20**, **21**), and a tetranitro derivative (**22**) was accomplished. The configurational assignment to the first four products was achieved by means of $^1$H NMR spectroscopy and an X-ray crystal structure analysis of **21**. The stereochemistries of the nitro-substituted cage molecules are discussed in terms of the mechanism of their formation and their densities, many of which are markedly enhanced. The structural features of the tetranitro-bishomopentaprismane **22** have also been elucidated by X-ray methods.

**Synthese von Hexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$.$0^{9,12}$]dodecan-5,11-dion und seine Umwandlung in Di-, Tri- und Tetranitro-1,3-bishomoprismane**

Sulfenylierung des Dianions von Dimethyl-tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-dien-5,12-dicarboxylat (**9**) mit Dimethyldisulfid ergab das *exo,exo*-Bis(methylthio)-Derivat **10a**. Nachfolgende Hydrolyse und oxidative Decarboxylierung führte zu Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]-dodeca-2,7-dien-5,12-dion (**4**), ein wichtiges Zwischenprodukt. Es wurde in das Bisketal **11** übergeführt und dieses zum doppelt funktionalisierten 1,3-Bishomopentaprismen **12** photolysiert. Nachfolgende saure Hydrolyse ergab die Titelverbindung **5**, woraus drei Dinitro- (**14**–**16**), zwei Trinitro- (**20**, **21**) und ein Tetranitro-Derivat (**22**) erhalten wurden. Die Konfigurationszuordnung der ersten vier Produkte erfolgte $^1$H-NMR-spektroskopisch und durch Röntgenstrukturanalyse von **21**. Die Stereochemie der Nitro-substituierten Käfigmoleküle wird aufgrund ihrer Bildung und ihrer Dichte diskutiert, die in vielen Fällen erhöht ist. Auch von Tetranitro-bishomopentaprisman **22** wurden die strukturellen Eigenschaften durch eine Röntgenstrukturanalyse erhellt.

The "domino Diels-Alder reaction"[2] is a two-stage cycloaddition process that results in the formation of four new C–C bonds. Intricate polycyclic structures not readily accessible by other means result[3–8]. From the standpoint of synthetic utility, the methodology has found application in the expedient preparation of


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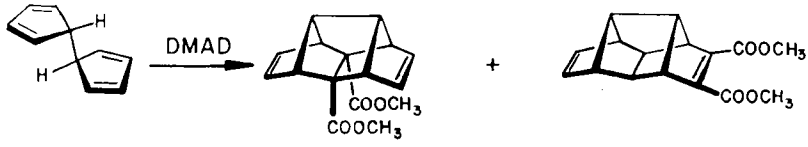
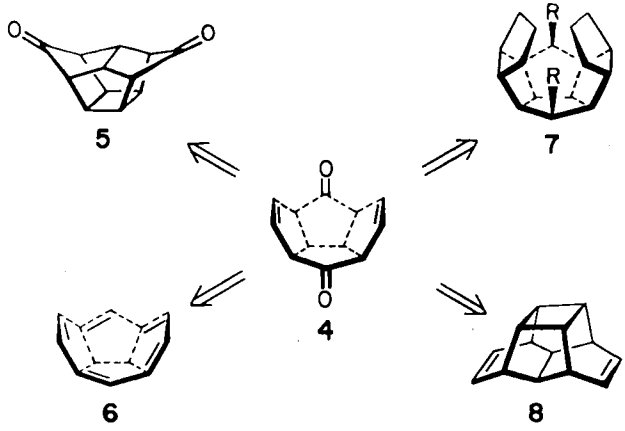
triquinacene[9], several $(CH)_{12}$ hydrocarbons[10], $C_{16}$-hexaquinacene[11], the pentagonal dodecahedrane[12], and several of its derivatives[13]. The condensation of 9,10-dihydrofulvalene (**1**) with dimethyl acetylenedicarboxylate (DMAD) to give diesters **2** and **3** possesses several particularly valuable features including the rapid construction of a caged polycyclopentanoid network having highly oxygenated substituents at quite different sites.




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

During the last several years, numerous applications of **2** to the construction of several higher polyquinane systems have been reported in the context of our dodecahedrane effort[14]. The present study demonstrates a new synthetic role for **2**, *viz.* as a precursor to the $C_{2v}$-symmetric $C_{12}$-diketone **4**[15]. As shown in the scheme, this tetraquinane holds considerable promise as a potential precursor to 1,3-bishomopentaprismanes (**5**), semi-spheroidal ethanediylidene [10]annulenes (**6**), and additional attractive targets (e.g., **7** and **8**). We also describe herein the transformation of **4** into **5**. Two other research groups have also recently gained access to one or both of these dicarbonyl compounds. Details of the *Mehta* approach have already been published[16]. The *Prinzbach* route to **5** differs significantly from either of the other two and complete details of the research carried out in Freiburg are being published alongside this report by prior agreement[17].

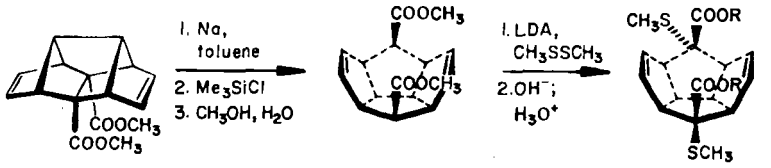



As part of a larger program directed toward the synthesis of polynitro caged molecules[18], the conversion of **5** into potentially energetic compounds of this type

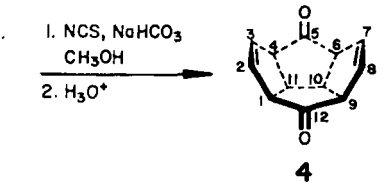
became desirable. Finally, stereochemical issues associated with the latter transformations are addressed.

## I. Synthesis of Diketone 4

The ease with which **2** undergoes reductive cleavage of its central bond in the presence of sodium metal has previously been documented[19]. Although the resulting dianion could be directly sulfenylated, it proved more efficient to transform **2** into its dihydro derivative **9** (95%) and to effect independent condensation with dimethyl disulfide under more strictly controlled conditions. For the usual steric reasons, entry of the methylthio substituents in **10a** is assumed to be relegated exclusively to the *exo* surface[13,14]. The yield of crystalline **10a**, although varying appreciably from one experiment to the next, peaked at 61%. Since the major by-product was the monosulfenylated diester, which in turn could also be transformed into **10a**, good overall efficiency (90 + %) could repeatedly be realized at this stage.




**2** **9** **10a**, R=$CH_3$ **b**, R=H



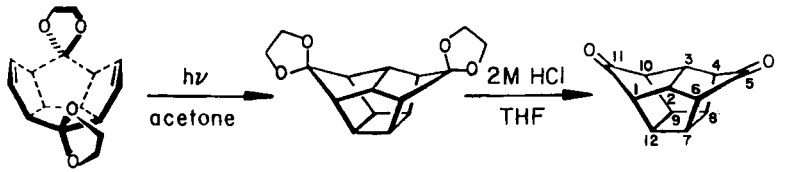

**4**

The highly hindered nature of the methoxycarbonyl groups in **10a** hampered neither saponification to dicarboxylic acid **10b** with potassium hydroxide in aqueous methanol (100%) nor the subsequent oxidative decarboxylation with *N*-chlorosuccinimide in buffered methanol[20]. Acidic hydrolysis of the resulting diketal provided **4** (55%). The inherent $C_{2v}$ symmetry of **4** was immediately obvious upon inspection of its $^1H$ (three absorptions) and $^{13}C$ NMR (four line) spectra.

## II. Conversion of 4 to 5

Having defined an expedient route to **4**, we next turned our attention to construction of a cyclobutane ring by [2 + 2] closure of its isolated $\pi$ bonds. Dreiding models of **4** reveal that these unsaturated centers are relatively distant. Clearly, their mutual proximity must be enhanced if photocycloaddition is to be satisfac-

torily implemented and the 1,3-bishomopentaprismane framework produced. In addition, possible undesirable side reactions such as oxa-di-π-methane rearrangements had to be rendered inoperative. It so happens that intermediate formation of bisketal **11** (92%) nicely resolves both potential complications. Thus, as the two dioxolane rings in **11** seek to avoid nonbonded steric interactions, the respective oxygenated tetraquinane carbon atoms move as distant as possible. Linked to this conformational flexing is a concurrent compression of the π bonds. As a result, construction of **12** proceeds smoothly (98%) when irradiation is performed in acetone at 350 nm.

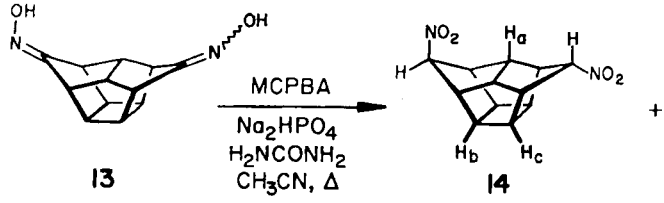



**11** **12** **5**

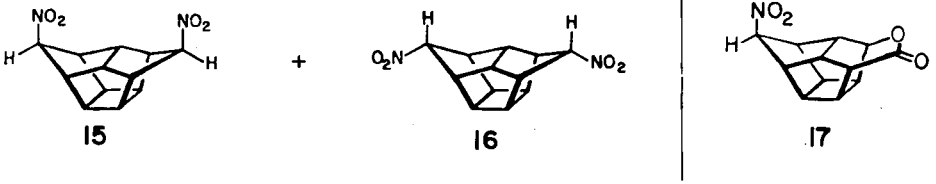
Photoproduct **12** is characterized by a six-line $^{13}C$ NMR spectrum and by a $^{1}H$ NMR spectrum lacking vinyl proton absorptions and showing resonances characteristic of a strained caged structure (see Experimental Section). Hydrolysis of **12** with 2 M hydrochloric acid in refluxing tetrahydrofuran proceeded slowly (105 h) but efficiently (95%) to deliver **5** whose structure and high symmetry was once again spectroscopically evident.

## III. Elaboration of the Polynitro-1,3-bishomopentaprismanes

From among the relatively few methods available for transforming a carbonyl group into a nitro substituent, that developed by *Emmons* and *Pagano*[21] appeared most serviceable. However, when oxidation of dioxime **13** with trifluoroperacetic acid proved unsatisfactory[22], recourse was made instead to buffered *m*-chloroperbenzoic acid (MCPBA) in hot acetonitrile. The effectiveness of this reagent




**13** **14**



**15** **16** **17**

combination is evident from the data in Table 1. These reactions are claimed to proceed by oxidation to the nitronic acid and subsequent isomerization to the thermodynamically more stable nitro product. To our knowledge, the stereochemistry of this process has not been previously scrutinized. Consequently, the distribution of **14**–**16** was of more than passing interest. The three isomeric dinitro compounds could be readily obtained in pure form by medium pressure liquid chromatography (MPLC) on silica gel. Analytical scale experiments failed to detect any tendency for epimerization under the conditions of separation. Consequently, it is assumed that the relative amounts of **14**–**16** reflect kinetic control.

$$R_2C{=}NOH \xrightarrow{RCO_3H} R_2C{=}NO_2H \longrightarrow R_2CHNO_2$$

Table 1. Product distributions in the MCPBA oxidation of **13**

| Run | Overall yield, % | Percent composition 14 | 15 | 16 |
|---|---|---|---|---|
| 1 | 16.7 | 51.6 | 27.4 | 21.0 |
| 2 | 19.5 | 48.7 | 30.2 | 21.1 |
| 3 | 22.9 | 50.3 | 26.0 | 23.7 |
| 4 | 20.9 | 49.4 | 25.3 | 25.3 |

Identification of **14** was made simple by virtue of its unique $C_s$ symmetry. Quite unlike the more highly symmetric **15** and **16** which are each characterized by four $^{13}C$ NMR peaks, **14** shows seven carbon signals (Figure 1). Configurational assignment to isomers **15** and **16** was arrived at on the basis of spectral analysis. Additional confirmation was derived from X-ray crystal structure analysis of a trinitro-1,3-bishomopentaprismane (see below). It has been recognized for some

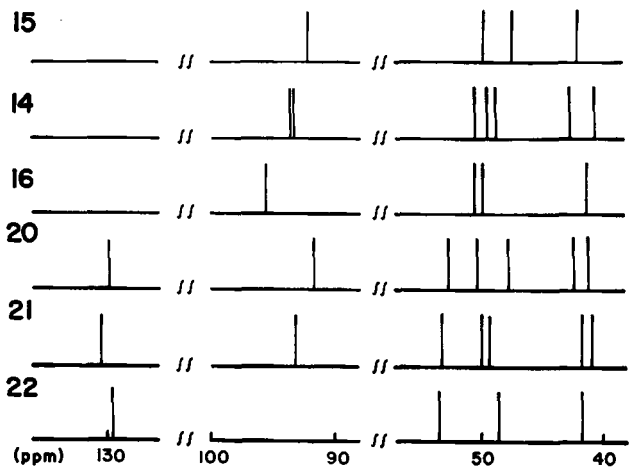



Figure 1. Schematic bar graph of $^{13}C$ chemical shifts for nitro-substituted 1,3-bishomopentaprismanes **14**–**16** and **20**–**22**

time that a nitro group exerts a shielding zone normal to the plane formed by the nitrogen and oxygen atoms[23]; in this respect, nitro compares closely to the carbonyl group. Molecular models of **14**–**16** suggested that appreciable diamagnetic anisotropy effects should operate on $H_a$ and $H_b/H_c$ (see **14** for designation) when the nitro group is *syn* oriented. As seen in Figure 2, the chemical shift differences between **14**–**16** are substantial. The simplest explanation for the respective appearances in **15** and **16** of $H_a$ at δ 2.72 and 3.39, and of $H_b/H_c$ at δ 3.00 (3.06)[24] and 2.88 is that the more upfield protons reside within the nitro shielding cones.

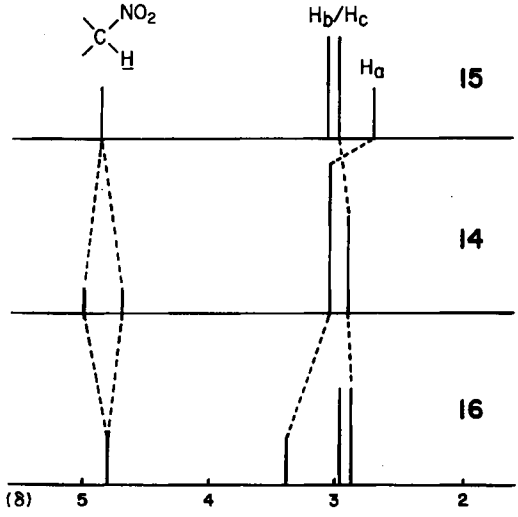


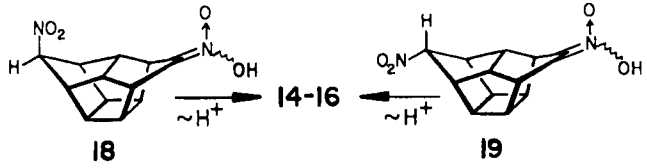

Figure 2. Schematic bar graph of $^1H$ chemical shifts for **14**–**16**

Long-range diamagnetic anisotropy effects are also in evidence. Thus, while the α-nitro protons in **15** and **16** appear at δ 4.90 and 4.81, respectively, those in **14** (δ 4.71, 5.01) fall outside this relatively narrow absorption range *in opposite directions.*

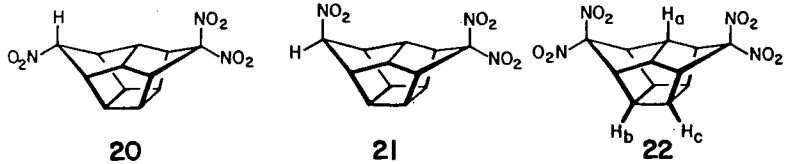
The relatively low composite yield of **14**–**16** is due in part to the formation of nitro lactone **17** (>15%). This substance can arise by several pathways; elucidation of the precise mechanistic details has not been pursued.

The distribution of dinitro stereoisomers **14**–**16** is clearly statistical. The implication is that the putative nitronic acids **18** and **19** are initially formed in approximately equal amounts and that subsequent tautomeric proton shift within these intermediates is similarly controlled by closely comparable transition state energies. To the extent that these activated complexes resemble the products, we are led to the working hypothesis that a nitro group has very similar energetic demands whether oriented quasi-axially or quasi-equatorially on a 1,3-bishomopentaprismane framework. However, the inefficiency of the oxidative process and

concurrent production of **17** are necessarily strong deterrents against accepting this conclusion *carte-blanche*. Equilibration experiments were not undertaken.




**18** **19**




**20** **21** **22**

In order to heighten the number of nitro groups, the **14**–**16** mixture was subjected to the anionic nitrating conditions of *Kornblum, Singh,* and *Kelly*[25]. Dropwise addition of a solution of the dinitro compounds in alkaline (NaOH) methanol to a two-phase (ether-water) solution of sodium nitrite and potassium ferricyanide afforded **20**–**22** in isolated yields of 33, 18, and 16%. That complete conversion to **22** did not result may be a reflection of the low solubility of **20** and **21** and/or incomplete formation of their corresponding monoanion. Similar incomplete conversion to the tetranitro derivative was observed starting directly from **20** and **21**.

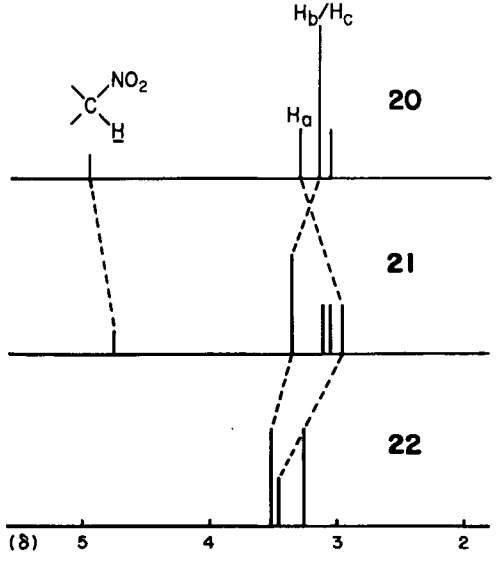
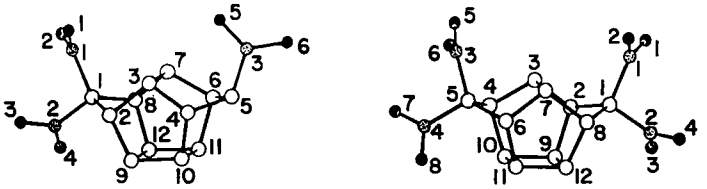



Figure 3. Schematic bar graph of $^1$H chemical shifts for **20**–**22**

The NMR spectra of **22** reflect its $C_{2v}$ symmetry. In $CDCl_3$ at 300 MHz, three protons are seen at δ 3.51 ($H_b$, $H_c$), 3.47 ($H_a$), and 3.28 (Figure 3) having a relative area distribution of 2:1:2. The four carbon types resonate in the same solvent at 129.23, 53.26, 48.53, and 41.70 ppm. Compared to **22**, the $H_a$ protons in **20** and **21** appear to higher field (δ 3.34 and 2.97, respectively). That the signal of $H_a$ in **21** appears at the highest field position within the triad is nicely accommodated by the magnetic anisotropy model, provided that the illustrated secondary nitro configuration is in place. This stereochemical conclusion is reinforced by the fact that $H_b/H_c$ in **20** is shielded relative to the corresponding absorption in **21** (Figure 3). However, because the locations of the $H_a$ and $H_b/H_c$ peaks in **22** do not follow the expected pattern, an X-ray crystal structure analysis of **21** was undertaken to provide irrefutable proof of stereochemistry.

As can be seen from Figure 4a, the secondary nitro group in **21** occupies the quasi-axial site in agreement with earlier conclusions based upon shielding phenomena. The seemingly anomalous position of the $H_b/H_c$ absorption in **22** must therefore again be due to long-range magnetic anisotropy contributions arising from the multiple nitro groups. In order to rule out possible conformational differences adopted by the quasi-equatorial nitro groups in **22**, its three-dimensional structural features were also elucidated by X-ray methods. A comparison of the drawings found in Figures 4a and 4b indicates any alterations in dihedral angle to be small. However, even at low temperature the nitro groups show high anisotropic motion. Such factors could bear directly on the chemical shift changes observed.

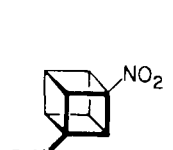


a b

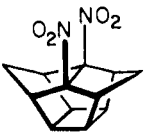
Figure 4. Side view perspective drawings of the molecular structures of **21** and **22** showing the numbering schemes utilized in the X-ray study

One additional feature of the polynitro-1,3-bishomopentaprismanes is deserving of emphasis. 1,4-Dinitrocubane (**23**)[26] and the vicinally dinitro-substituted homologue **24**[18] have previously been shown to possess high densities, presumably as the end result of heightened strain energy and structural compactness[27]. The *Kitaigorodsky* method for the calculation of molecular density[28], as modified by input of improved data[29], suggests that density should increase appreciably as any caged carbon framework experiences incrementally greater substitution by nitro groups[30]. However, the group additivity rules are not capable of accurately delineating possible differences arising from stereoisomers. Consequently, the ques-

tion of whether epimers can engage in comparably close molecular packing holds interest.




**23**




**24**

For **21** and **22**, densities of 1.69 and 1.73 g $cm^{-3}$ were calculated from the respective cell content and size. The flotation method (aqueous cesium chloride solution) was utilized for direct measurement of the other density values. The data are compiled in Table 2. Explicitly evident in this listing are several highly relevant facts. The first is seen in the dinitro series, where **16** is significantly more dense than either of its epimers. The derived implication is that attachment of nitro substituents to this carbocyclic framework from the quasi-equatorial direction permits more effective packing of molecules within the unit cell. Additional credence is derived from the ϱ values of the pair of trinitro-1,3-bishomopentaprismanes which reveal **20** to be more dense than **21**. Since **16** and **20** have densities equal to that of tetranitro compound **22**, it is clear that the multiplication of nitro groups is not the only means to increase density as earlier assumed[28,29]. Rather, the present investigation discloses that the judicious stereodisposition of fewer nitro groups can achieve the identical result. This previously unrecognized stereochemical facet of molecular density is continuing to receive attention in this laboratory.

Table 2. Densities of polynitro caged molecules[a]

| Compd. | ϱ, g $cm^{-3}$ | Compd. | ϱ, g $cm^{-3}$ |
|---|---|---|---|
| **23** | 1.66[b,c] | **16** | 1.75 |
| **24** | 1.63[c] | **20** | 1.75 |
| **14** | 1.58 | **21** | 1.69[c] |
| **15** | 1.62 | **22** | 1.76, 1.73[c] |

[a] Values determined by the flotation method (in aqueous CsCl) unless otherwise noted. – [b] Determined by the flotation method in aqueous KI solution. – [c] Calculated from the crystallographic data.

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## Experimental

IR Spectra: Perkin-Elmer Model 1320. – $^1$H and $^{13}$C NMR Spectra: Bruker WM-300. – MS: Kratos MS-30. – Melting points: uncorrected. – Elemental analyses: Scandinavian Microanalytical Laboratory, Box 25, Herlev, Denmark.

*Dimethyl exo-5,exo-12-Bis(methylthio)tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dicarboxylate* (**10a**): A solution of diester **9**[19] (16.77 g, 61.1 mmol) in anhydrous tetrahydrofuran (200 ml) was added dropwise under nitrogen to a cold (−78°C), magnetically stirred solution of lithium diisopropylamide (3 eq) in the same solvent (200 ml) during 15 min. The reaction mixture was stirred for 3 h at −78°C and 1 h at 0°C. Dimethyl disulfide (15.6 ml, 174 mmol, freshly distilled from $CaH_2$) was introduced dropwise at 0°C. Stirring was maintained for 2 h at 0°C and during 3 h as slow warming to room temperature occurred. The solution was poured into 500 ml of 1 M $NaH_2PO_4$ and the product was extracted into ethyl acetate (3 × 30 ml). The combined organic layers were washed with saturated brine, dried, and evaporated to leave 22.5 g of residue. Crystallization from ethyl acetate afforded pure **10a** as colorless crystals. Yield 13.66 g (61%), m.p. 196–197°C. – IR (KBr) 3075, 2980, 1730, 1440, 1270, 1070, 750 $cm^{-1}$. – $^1$H NMR (300 MHz, $CDCl_3$): δ = 5.59 (s, 4H), 3.77 (br s, 8H), 3.45 (m, 4H), 2.14 (s, 6H). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 171.41, 135.27, 61.19, 57.80, 51.84, 49.66, 13.41.

$C_{18}H_{22}O_4S_2$ (366.5) Calcd. C 59.00 H 6.06 Found C 58.78 H 6.06

The mother liquor can be resubjected to the sulfenylation conditions described and the total yield of **10a** increased to 90–94% in this fashion.

*Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dione* (**4**): A 60.0 g (0.164 mol) sample of **10a** was added to a solution of potassium hydroxide (184 g, 3.28 mol) in a mixture of 205 ml of water and 1025 ml of methanol. The stirred reaction mixture was heated at the reflux temperature under nitrogen for 18 h. Approximately 1 l of methanol was removed under reduced pressure, whereupon the residue was poured into 1 l of water and acidified to pH 1 with conc. hydrochloric acid. The precipitated acid **10b** was collected, washed with water, and dried azeotropically in toluene. Yield 55.4 g (100%).

A suspension of 33.0 g (97.5 mmol) of **10a** in 1430 ml of methanol containing 56.9 g (0.68 mol) of sodium hydrogen carbonate was heated at 35°C for 30 min with vigorous stirring. Following cessation of gas evolution, the reaction mixture was cooled to 20°C prior to the addition of *N*-chlorosuccinimide (65.2 g, 0.487 mol) in six portions during 15 min. After 6 h of stirring, 1430 ml of 0.5 M $Na_2SO_3$ was added and 1.2 l of methanol was removed under reduced pressure. The product was extracted into dichloromethane (5 × 300 ml) and ether (600 ml). The combined organic phases were treated with 500 ml of 10% hydrochloric acid and stirred for 4 h. The organic phase was separated, washed with water, dried, and evaporated. The residue was purified by HPLC on silica gel. Yield 10.0 g (55%), colorless cubes from ethyl acetate, m.p. 222–223°C. – IR (KBr) 3010, 2935, 1735, 1680, 1305, 1200, 965, 625 $cm^{-1}$. – $^1$H NMR (300 MHz, $CDCl_3$): δ = 5.68 (t, *J* = 4.0 Hz, 4H), 3.90 (m, 2H), 3.63 (dd, *J* = 4.0, 2.5 Hz, 4H). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 214.64, 133.52, 62.67, 43.06.

$C_{12}H_{10}O_2$ (186.2) Calcd. C 77.39 H 5.42 Found C 77.24 H 5.42

*Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene-5,12-dione Bis(ethylene acetal)* (**11**): A solution of **4** (930 mg, 0.50 mmol), ethylene glycol (310 mg, 5.0 mmol), and *p*-toluenesulfonic acid monohydrate (4.8 mg) in 13 ml of benzene was heated at the reflux temperature for 1.5 h under a Dean Stark trap filled with molecular sieves. The cooled reaction mixture was washed with 20 ml of 10% sodium hydroxide solution and 3 × 10 ml of water prior to drying and solvent evaporation. The brownish residue was purified by MPLC on silica gel

(elution with 25% ethyl acetate in petroleum ether). Yield 125 mg (92%), colorless prisms from hexane, m.p. 135–136°C. – IR (KBr) 3060, 1105 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 5.54 (br s, 4H), 3.98 (s, 8H), 3.4–3.3 (m, 2H), 3.25–3.0 (m, 4H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 133.77, 116.08, 65.29, 63.82, 59.07, 45.87. – MS: *m/z* = 274.12 ($M^+$).

$C_{16}H_{18}O_4$ (274.3) Calcd. C 70.06 H 6.61 Found C 69.87 H 6.68

*Hexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{4,8}$.0$^{9,12}$]dodecane-5,11-dione Bis(ethylene acetal)* (**12**): A solution of **11** (25 mg, 0.091 mmol) in 0.6 ml of acetone was placed in an NMR tube, blanketed with nitrogen, and irradiated with 350 nm light in a Rayonet reactor for 2.5 h. The solvent was evaporated and the product was isolated by MPLC on silica gel. Yield 24.6 mg (98%), colorless prisms from hexane, m.p. 118.5–120°C. – IR (KBr) 2980, 2880, 1380, 1120 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.89 (dd, *J* = 4.1, 4.4 Hz, 4H), 3.82 (dd, *J* = 4.1, 4.4 Hz, 4H), 2.80 (m, 6H), 2.01 (br s, 4H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 124.06, 65.10, 64.91, 50.03, 47.73, 42.49. – MS: *m/z* = 274.12 ($M^+$).

*Hexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{4,8}$.0$^{9,12}$]dodecane-5,11-dione* (**5**): Diketal **12** (206 mg, 0.75 mmol) was added to 4 ml of tetrahydrofuran containing 2.0 ml of 2 M HCl. The mixture was heated at the reflux temperature for 105 h, poured into 20 ml of water, and neutralized by addition of sodium hydrogen carbonate solution. The product was extracted into dichloromethane (3 × 30 ml) and the combined organic layers were dried and evaporated. The residue was purified by MPLC on silica gel. Yield 133 mg (95%), colorless prisms from ethyl acetate, m.p. 228.5–230°C. – IR (KBr) 1767, 1380, 1280, 1135 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.26 (br s, 4H), 3.15 (br s, 2H), 2.25 (br s, 4H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 210.49, 48.81, 42.30, 41.66. – MS: *m/z* = 186.07 ($M^+$).

$C_{12}H_{10}O_2$ (186.2) Calcd. C 77.40 H 5.41 Found C 77.41 H 5.54

*Hexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{4,8}$.0$^{9,12}$]dodecane-5,11-dione Dioxime* (**13**): A suspension of **5** (884 mg, 4.75 mmol), hydroxylamine hydrochloride (3.30 g, 47.5 mmol), and anhydrous sodium acetate (7.78 g, 95 mmol) in 88 ml of methanol was stirred at room temp. for 19.5 h. The reaction mixture was poured into 700 ml of water and extracted with ethyl acetate (10 × 300 ml). The combined organic layers were washed with water (50 ml) and brine (50 ml), dried, and evaporated to give **13** as a colorless solid residue. Yield 962 mg (94%). – MS: *m/z* = 216.09 ($M^+$).

*Oxidation of* **13**: *5,11-Dinitrohexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{4,8}$.0$^{9,12}$]dodecanes* **14**–**16**: A stirred suspension of **13** (432 mg, 2.00 mmol), finely powdered urea (81 mg), and finely powdered sodium monohydrogen phosphate (3.12 g) in 8 ml of acetonitrile was heated to the reflux temperature. *m*-Chloroperoxybenzoic acid (1.73 g of 80% purity, 8.02 mmol) was added in small portions to this mixture during 55 min. Upon completion of the addition, heating was continued for 2 h prior to cooling. Dichloromethane (30 ml) was added and the precipitate that formed was removed by filtration and washed with additional solvent (3 × 20 ml). The combined filtrates were evaporated and the residue was redissolved in dichloromethane (450 ml) and the solution was washed with 5% sodium hydroxide solution (75 ml) and water (75 ml) prior to drying. Concentration left a viscous pale yellow residue that was separated into its three components by MPLC on silica gel (elution with ethyl acetate/petroleum ether 1:5).

For **14**: 57.2 mg (12%), colorless needles from ethyl acetate/petroleum ether, m.p. 118–119°C. – IR (KBr) 2995, 1528, 1379, 1289, 766 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 5.01 (s, 1H), 4.71 (s, 1H), 3.06 (br s, 6H), 2.91 (br s, 4H). – $^{13}C$-NMR (75 MHz, $CDCl_3$): δ = 93.48, 93.33, 50.22, 49.27, 48.55, 42.51, 40.51.

$C_{12}H_{12}N_2O_4$ (248.2) Calcd. C 58.06 H 4.87 Found C 58.03 H 5.20

For **15**: 29.5 mg (5.9%), colorless crystals from ethyl acetate/petroleum ether, m.p. 192–193°C. – IR (KBr) 1530, 1375, 1293, 785 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.90 (t, *J* = 1.6 Hz, 2H), 3.09 (br s, 4H), 3.00 (br s, 4H), 2.72 (br s, 2H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 92.14, 49.54, 47.01, 41.84. – MS: no molecular ion peak.

For **16**: 26.9 mg (5.4%), colorless prisms from ethyl acetate/petroleum ether, m.p. 134.5–136°C. – IR (KBr) 1530, 1380, 1295, 755 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.81 (s, 2H), 3.39 (br s, 2H), 2.97 (br s, 4H), 2.88 (br s, 4H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 95.50, 50.30, 49.71, 41.17. – MS: no molecular ion peak.

An increase in solvent polarity also eluted 86.9 mg (15.4%) of **17**. – IR (KBr) 1755, 1740, 1535, 1385 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 5.00 (t, *J* = 1.6 Hz, 1H), 4.83 (dd, *J* = 4.9, 5.4 Hz, 1H), 3.29 (dd, *J* = 13.4, 6.0 Hz, 1H), 3.15–2.95 (m, 4H), 2.95–2.80 (m, 2H), 2.80–2.70 (m, 2H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 172.88, 90.49, 79.77, 49.27, 45.51, 44.17, 43.36, 42.40, 42.06, 40.01, 37.44, 35.61. – MS: no molecular ion peak.

*Oxidative Nitration of* **14–16**: *5,5,11-Trinitro-* (**20, 21**) *and 5,5,11,11-Tetranitrohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{4,8}$.$0^{9,12}$]dodecanes* (**22**): A mixture of the epimeric dinitro-1,3-bishomopentaprismanes (100 mg, 0.40 mmol) in methanol (1.7 ml) was added to a solution of sodium hydroxide (44.3 mg) in water (2.1 ml) and this mixture was stirred under nitrogen for 30 min. The resulting clear yellow solution was added dropwise during 5 min to a vigorously stirred two-phase mixture containing 1.45 g (4.43 mmol) of potassium ferricyanide, 0.62 g (8.86 mmol) of sodium nitrite, 8.4 ml of water, and 17 ml of ether. After 1 h of stirring, the organic phase was separated and the aqueous layer was extracted with ether (2 × 30 ml). The organic solutions were combined, washed with 10 ml of water, dried, and evaporated. The products were separated by MPLC on silica gel (elution with ethyl acetate/petroleum ether 1:5).

For **20**: 38.6 mg (33%), colorless prisms from ethyl acetate/petroleum ether, m.p. 145.5–147°C. – IR (KBr) 1570, 1540, 1378, 1325, 1293, 1280, 820, 797, 760 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.99 (s, 1H), 3.34 (br s, 2H), 3.18 (br s, 6H), 3.10 (br s, 2H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 129.80, 91.74, 52.52, 50.24, 47.63, 42.30, 41.05. – MS: no molecular ion peak.

For **21**: 21.2 mg (18%), colorless prisms from ethyl acetate/petroleum ether, m.p. 150.0–150.5°C. – IR (KBr) 1557, 1547, 1370, 1325, 829, 809, 798, 775, 759 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 4.77 (t, *J* = 1.7 Hz, 1H), 3.37 (br s, 4H), 3.12 (m, 2H), 3.06 (br s, 2H), 2.97 (br s, 2H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 130.94, 93.16, 53.03, 49.94, 49.30, 41.71, 40.92. – MS: no molecular ion peak. – X-Ray: see below.

For **22**: 21.6 mg (16%), colorless prisms from ethyl acetate/petroleum ether, m.p. 235–236°C. – IR (KBr) 1565, 1360, 1320, 1285, 823, 792, 771 $cm^{-1}$. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.51 (br s, 4H), 3.47 (br s, 2H), 3.28 (br s, 4H). – $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 129.23, 53.26, 48.53, 41.70. – MS: no molecular ion peak.

$C_{12}H_{10}N_4O_8$ (338.2) Calcd. C 42.61 H 2.98 Found C 42.98 H 3.18

*Oxidative Nitration of* **20** *and* **21**: A mixture of **20** and **21** (127 mg, 0.433 mmol) was dissolved under nitrogen into a solution of sodium hydroxide (29.6 mg, 0.736 mmol) in methanol (0.9 ml), water (1.1 ml), and tetrahydrofuran (1 ml). After 30 min of stirring, the clear yellow solution was added dropwise during 3 min to a vigorously stirred two-phase mixture containing sodium nitrite (131 mg, 4.51 mmol), potassium ferricyanide (633 mg, 2.26 mmol), water (5 ml), and tetrahydrofuran (9 ml). Following 1 h of stirring under nitrogen, the mixture was extracted with ether (4 × 40 ml). The remaining aqueous phase was acidified to pH 6 with acetic acid and extracted with dichloromethane (2 × 30 ml). The organic solutions were combined, washed with water (15 ml), dried, and evaporated.

Table 3. Fractional coordinates and anisotropic and isotropic temperature factors, respectively, with standard deviation for the non-hydrogen and hydrogen atoms of **21**. $T = \exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $2\beta_{12}$ | $2\beta_{13}$ | $2\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 0.0665(4) | 0.7924(3) | 0.3089(3) | 0.0069(9) | 0.0027(4) | 0.0031(4) | -0.001(1) | 0.002(1) | -0.0005(7) |
| C(2) | 0.2153(4) | 0.8370(2) | 0.2724(2) | 0.007(1) | 0.0030(5) | 0.0025(4) | -0.001(1) | 0.003(1) | 0.0007(7) |
| C(3) | 0.3348(4) | 0.7349(2) | 0.2912(2) | 0.0066(9) | 0.0029(5) | 0.0025(4) | -0.001(1) | 0.003(1) | -0.0006(7) |
| C(4) | 0.5194(4) | 0.7774(3) | 0.3401(3) | 0.007(1) | 0.0033(5) | 0.0032(5) | -0.001(1) | 0.004(1) | 0.0000(7) |
| C(5) | 0.6106(4) | 0.6922(3) | 0.4318(3) | 0.007(1) | 0.0032(5) | 0.0039(5) | 0.001(1) | 0.004(1) | -0.0005(8) |
| C(6) | 0.4741(4) | 0.6892(3) | 0.4929(3) | 0.007(1) | 0.0030(5) | 0.0029(4) | -0.000(1) | 0.002(1) | 0.0004(7) |
| C(7) | 0.3024(4) | 0.6731(2) | 0.3966(2) | 0.007(1) | 0.0024(4) | 0.0028(4) | -0.001(1) | 0.003(1) | -0.0000(7) |
| C(8) | 0.1681(4) | 0.7479(2) | 0.4264(2) | 0.0064(9) | 0.0030(4) | 0.0025(4) | -0.001(1) | 0.003(1) | 0.0003(7) |
| C(9) | 0.3073(4) | 0.9118(2) | 0.3749(3) | 0.008(1) | 0.0024(4) | 0.0034(5) | -0.001(1) | 0.003(1) | -0.0000(8) |
| C(10) | 0.4972(4) | 0.8746(2) | 0.4165(3) | 0.007(1) | 0.0027(4) | 0.0036(5) | -0.003(1) | 0.002(1) | -0.0009(8) |
| C(11) | 0.4657(4) | 0.8140(3) | 0.5219(2) | 0.007(1) | 0.0034(5) | 0.0026(4) | -0.001(1) | 0.001(1) | -0.0012(8) |
| C(12) | 0.2749(4) | 0.8507(2) | 0.4800(2) | 0.007(1) | 0.0027(4) | 0.0028(4) | -0.001(1) | 0.003(1) | -0.0014(7) |
| O(1) | -0.0136(4) | 0.6802(3) | 0.1433(2) | 0.015(1) | 0.0097(6) | 0.0050(4) | -0.009(1) | 0.007(1) | -0.0070(8) |
| O(2) | -0.1519(4) | 0.6608(3) | 0.2636(3) | 0.015(1) | 0.0089(5) | 0.0082(5) | -0.014(1) | 0.011(1) | -0.0056(9) |
| O(3) | -0.1483(5) | 0.9160(3) | 0.2159(3) | 0.024(1) | 0.0109(7) | 0.0068(5) | 0.020(2) | 0.007(1) | 0.0071(9) |
| O(4) | -0.0849(4) | 0.9087(3) | 0.3980(2) | 0.013(1) | 0.0087(6) | 0.0065(5) | 0.008(1) | 0.006(1) | -0.0032(8) |
| O(5) | 0.5407(4) | 0.5402(2) | 0.3044(3) | 0.013(1) | 0.0051(4) | 0.0083(5) | -0.000(1) | 0.005(1) | -0.0054(8) |
| O(6) | 0.7678(4) | 0.5287(3) | 0.4479(3) | 0.020(1) | 0.0064(5) | 0.0065(5) | 0.012(1) | 0.006(1) | 0.0026(8) |
| N(1) | -0.0407(3) | 0.7036(2) | 0.2312(2) | 0.0064(9) | 0.0044(4) | 0.0035(4) | -0.002(1) | 0.001(1) | -0.0008(7) |
| N(2) | -0.0662(4) | 0.8811(2) | 0.3088(3) | 0.0080(9) | 0.0041(5) | 0.0056(5) | 0.002(1) | 0.004(1) | 0.0010(8) |
| N(3) | 0.6419(4) | 0.5789(2) | 0.3900(3) | 0.011(1) | 0.0039(4) | 0.0052(5) | 0.002(1) | 0.008(1) | 0.0008(8) |

| Atom | x | y | z | B |
|---|---|---|---|---|
| H(21) | 0.191(5) | 0.874(3) | 0.194(3) | 1.0(6) |
| H(31) | 0.319(5) | 0.684(3) | 0.223(3) | 1.1(6) |
| H(41) | 0.569(5) | 0.799(3) | 0.279(3) | 1.0(6) |
| H(51) | 0.730(5) | 0.715(3) | 0.484(3) | 1.2(6) |
| H(61) | 0.493(5) | 0.635(3) | 0.561(3) | 1.0(6) |
| H(71) | 0.267(5) | 0.593(3) | 0.382(3) | 1.0(6) |
| H(81) | 0.097(5) | 0.714(4) | 0.478(3) | 1.3(6) |
| H(91) | 0.282(5) | 0.994(3) | 0.365(3) | 1.0(6) |
| H(101) | 0.588(5) | 0.936(3) | 0.425(3) | 1.1(6) |
| H(111) | 0.531(5) | 0.838(4) | 0.602(4) | 1.5(7) |
| H(121) | 0.228(5) | 0.896(3) | 0.534(3) | 1.3(6) |

Table 4. Bond lengths and angles in **21**

| A-B | (Å) | A-B | (Å) |
|---|---|---|---|
| C(1)-N(1) | 1.515(4) | C(7)-H(71) | 1.004(35) |
| C(1)-N(2) | 1.521(4) | C(7)-C(8) | 1.550(3) |
| C(1)-C(2) | 1.523(3) | C(8)-H(81) | 1.068(31) |
| C(1)-C(8) | 1.524(4) | C(8)-C(12) | 1.535(4) |
| C(2)-H(21) | 1.019(34) | C(9)-H(91) | 1.006(35) |
| C(2)-C(3) | 1.538(4) | C(9)-C(10) | 1.546(3) |
| C(2)-C(9) | 1.541(4) | C(9)-C(12) | 1.580(4) |
| C(3)-H(31) | 1.012(35) | C(10)-H(101) | 1.026(31) |
| C(3)-C(4) | 1.532(3) | C(10)-C(11) | 1.578(4) |
| C(3)-C(7) | 1.588(4) | C(11)-H(111) | 1.005(36) |
| C(4)-H(41) | 0.997(30) | C(11)-C(12) | 1.551(3) |
| C(4)-C(5) | 1.533(4) | C(12)-H(121) | 1.024(33) |
| C(4)-C(10) | 1.542(4) | N(1)-O(1) | 1.205(4) |
| C(5)-H(51) | 1.023(30) | N(1)-O(2) | 1.217(3) |
| C(5)-N(3) | 1.500(4) | N(2)-O(4) | 1.202(4) |
| C(5)-C(6) | 1.533(3) | N(2)-O(3) | 1.208(4) |
| C(6)-H(61) | 1.030(34) | N(3)-O(5) | 1.212(4) |
| C(6)-C(11) | 1.542(4) | N(3)-O(6) | 1.216(4) |
| C(6)-C(7) | 1.545(4) | | |

| A-B-C | (°) | A-B-C | (°) |
|---|---|---|---|
| N(1)-C(1)-N(2) | 102.4(2) | C(11)-C(6)-C(7) | 101.7(2) |
| N(1)-C(1)-C(2) | 114.8(2) | C(6)-C(7)-C(8) | 106.9(2) |
| N(1)-C(1)-C(8) | 113.1(3) | C(6)-C(7)-C(3) | 103.0(2) |
| N(2)-C(1)-C(2) | 113.3(3) | C(8)-C(7)-C(3) | 103.8(2) |
| N(2)-C(1)-C(8) | 115.1(2) | C(1)-C(8)-C(12) | 101.4(2) |
| C(2)-C(1)-C(8) | 98.7(2) | C(1)-C(8)-C(7) | 101.3(2) |
| C(1)-C(2)-C(3) | 102.1(2) | C(12)-C(8)-C(7) | 102.3(2) |
| C(1)-C(2)-C(9) | 101.2(2) | C(2)-C(9)-C(10) | 106.8(2) |
| C(3)-C(2)-C(9) | 102.3(2) | C(2)-C(9)-C(12) | 103.7(2) |
| C(4)-C(3)-C(2) | 107.5(2) | C(10)-C(9)-C(12) | 90.3(2) |
| C(4)-C(3)-C(7) | 103.3(2) | C(4)-C(10)-C(9) | 108.3(2) |
| C(2)-C(3)-C(7) | 103.4(2) | C(4)-C(10)-C(11) | 103.7(3) |
| C(3)-C(4)-C(5) | 105.3(2) | C(9)-C(10)-C(11) | 89.9(2) |
| C(3)-C(4)-C(10) | 101.6(2) | C(6)-C(11)-C(12) | 108.1(2) |
| C(5)-C(4)-C(10) | 100.1(2) | C(6)-C(11)-C(10) | 103.0(2) |
| N(3)-C(5)-C(4) | 116.4(2) | C(12)-C(11)-C(10) | 90.2(2) |
| N(3)-C(5)-C(6) | 112.2(3) | C(8)-C(12)-C(11) | 107.3(2) |
| C(4)-C(5)-C(6) | 96.6(2) | C(8)-C(12)-C(9) | 103.8(2) |
| C(5)-C(6)-C(11) | 100.6(2) | C(11)-C(12)-C(9) | 89.7(2) |
| C(5)-C(6)-C(7) | 104.8(2) | | |

$^1$H NMR analysis of the solid residue showed the relative proportions of **20**, **21**, and **22** to be 27.7, 16.3, and 56.0%, respectively.

*X-Ray Crystal Structure Analyses of* **21** *and* **22**: The crystals are colorless. The space groups were determined by preliminary Weissenberg photographs with Cu-$K_\alpha$ radiation. Determination of the lattice parameters and intensity measurements were made with a NONIUS CAD-4 diffractometer using graphite monochromatized Mo-$K_\alpha$ radiation ($\lambda$ = 0.71065 Å). The cell parameters were calculated by a least-squares procedure from reflections determined by the NONIUS peak hunting procedure in the range $6° < 2\Theta < 20°$. Independent reflections in the range $2° \leq 2\Theta \leq 60°$ were measured at $T = -123$ (3)°C by the $\omega-2\Theta$ scan technique. After every 200 reflections, the orientation of the crystals was controlled and after every 3.3 h, the intensity was checked. No significant deviation

Table 5. Fractional coordinates and anisotropic temperature factors with standard deviation for the non-hydrogen atoms of **22**. $T = \exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $2\beta_{12}$ | $2\beta_{13}$ | $2\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1A) | 0.8606(4) | 0.4372(4) | 0.4528(4) | 0.0130(6) | 0.0098(4) | 0.0190(6) | 0.0044(8) | 0.0031(9) | -0.0178(8) |
| O(2A) | 1.0388(6) | 0.4852(3) | 0.3443(4) | 0.0309(9) | 0.0049(3) | 0.0089(4) | -0.0035(9) | 0.0048(9) | -0.0040(5) |
| O(3A) | 0.9155(4) | 0.1601(4) | 0.5767(3) | 0.0174(6) | 0.0115(4) | 0.0043(3) | -0.0075(8) | 0.0017(6) | -0.0001(5) |
| O(4A) | 1.1001(4) | 0.2595(4) | 0.5798(3) | 0.0112(5) | 0.0159(5) | 0.0048(3) | -0.0018(8) | -0.0061(6) | -0.0022(6) |
| O(5A) | 0.8796(3) | 0.4155(3) | -0.0292(3) | 0.0080(4) | 0.0049(2) | 0.0064(3) | 0.0023(5) | -0.0014(5) | 0.0015(4) |
| O(6A) | 1.0847(4) | 0.3841(3) | -0.0946(3) | 0.0108(4) | 0.0066(3) | 0.0059(3) | -0.0020(6) | 0.0060(5) | 0.0033(4) |
| O(7A) | 0.9082(4) | 0.1609(3) | -0.0957(3) | 0.0117(5) | 0.0080(3) | 0.0062(3) | 0.0011(6) | -0.0055(6) | -0.0071(5) |
| O(8A) | 1.1098(3) | 0.0907(3) | -0.0262(3) | 0.0076(4) | 0.0067(3) | 0.0081(3) | 0.0005(5) | 0.0034(5) | -0.0078(5) |
| N(1A) | 0.9604(5) | 0.4143(3) | 0.4001(3) | 0.0139(6) | 0.0057(3) | 0.0052(3) | 0.0027(7) | -0.0061(7) | -0.0058(5) |
| N(2A) | 1.0014(4) | 0.2306(3) | 0.5316(3) | 0.0085(4) | 0.0071(3) | 0.0038(3) | 0.0025(6) | -0.0007(5) | -0.0020(5) |
| N(3A) | 0.9857(3) | 0.3559(3) | -0.0315(3) | 0.0073(4) | 0.0040(3) | 0.0031(2) | -0.0025(5) | -0.0015(5) | -0.0002(4) |
| N(4A) | 1.0066(4) | 0.1558(3) | -0.0308(3) | 0.0072(4) | 0.0045(3) | 0.0043(3) | -0.0027(5) | 0.0021(5) | -0.0027(4) |
| C(1A) | 0.9883(4) | 0.2853(3) | 0.4036(3) | 0.0075(5) | 0.0040(3) | 0.0037(3) | 0.0012(6) | -0.0014(6) | -0.0013(5) |
| C(2A) | 0.8754(4) | 0.2344(3) | 0.3414(3) | 0.0055(4) | 0.0044(3) | 0.0032(3) | 0.0007(5) | 0.0000(5) | -0.0013(5) |
| C(3A) | 0.9030(4) | 0.2974(3) | 0.2148(3) | 0.0055(4) | 0.0030(3) | 0.0033(3) | 0.0012(5) | -0.0011(5) | -0.0014(4) |
| C(4A) | 0.8807(4) | 0.2081(3) | 0.1405(3) | 0.0042(4) | 0.0036(3) | 0.0035(3) | -0.0010(5) | 0.0010(5) | -0.0011(4) |
| C(5A) | 0.9978(4) | 0.2371(3) | 0.0516(3) | 0.0054(4) | 0.0031(3) | 0.0032(3) | -0.0010(5) | -0.0000(5) | -0.0013(4) |
| C(6A) | 1.1194(4) | 0.2278(3) | 0.1354(3) | 0.0042(4) | 0.0036(3) | 0.0039(3) | -0.0007(5) | 0.0000(5) | -0.0006(4) |
| C(7A) | 1.0680(4) | 0.3120(3) | 0.2096(3) | 0.0054(4) | 0.0030(3) | 0.0036(3) | -0.0012(5) | -0.0013(5) | -0.0004(4) |
| C(8A) | 1.1136(4) | 0.2576(3) | 0.3344(3) | 0.0058(4) | 0.0044(3) | 0.0034(3) | -0.0010(6) | -0.0017(5) | -0.0010(5) |
| C(9A) | 0.9338(4) | 0.1103(3) | 0.3451(3) | 0.0055(4) | 0.0032(3) | 0.0042(3) | -0.0005(5) | 0.0013(5) | -0.0003(4) |
| C(10A) | 0.9371(4) | 0.0933(3) | 0.2196(3) | 0.0053(4) | 0.0029(3) | 0.0039(3) | -0.0011(5) | 0.0012(5) | -0.0007(4) |
| C(11A) | 1.1003(4) | 0.1074(3) | 0.2169(3) | 0.0052(4) | 0.0032(3) | 0.0043(3) | 0.0011(5) | 0.0010(5) | -0.0003(4) |
| C(12A) | 1.0970(4) | 0.1257(3) | 0.3416(3) | 0.0061(4) | 0.0039(3) | 0.0033(3) | 0.0010(6) | -0.0002(5) | 0.0008(4) |
| O(1B) | 0.5774(4) | 0.3782(3) | 0.3800(3) | 0.0125(5) | 0.0079(3) | 0.0080(3) | 0.0105(6) | 0.0009(6) | 0.0030(5) |
| O(2B) | 0.3861(4) | 0.4573(3) | 0.4220(3) | 0.0139(5) | 0.0083(3) | 0.0054(3) | 0.0050(6) | 0.0083(6) | 0.0037(5) |
| O(3B) | 0.5869(3) | 0.4444(3) | 0.1043(3) | 0.0083(4) | 0.0095(3) | 0.0072(3) | 0.0014(6) | 0.0024(5) | -0.0098(5) |
| O(4B) | 0.3733(4) | 0.4073(3) | 0.1544(3) | 0.0095(4) | 0.0091(3) | 0.0087(3) | -0.0067(6) | 0.0022(6) | -0.0107(6) |
| O(5B) | 0.6037(4) | 0.8504(4) | 0.4759(3) | 0.0157(6) | 0.0112(4) | 0.0064(3) | 0.0064(8) | -0.0082(7) | -0.0075(6) |
| O(6B) | 0.3932(4) | 0.9202(4) | 0.4564(3) | 0.0106(5) | 0.0138(5) | 0.0092(4) | -0.0027(7) | 0.0052(7) | -0.0130(7) |
| O(7B) | 0.6185(4) | 1.0693(3) | 0.2648(4) | 0.0111(5) | 0.0064(3) | 0.0166(5) | -0.0062(6) | -0.0024(8) | -0.0005(7) |
| O(8B) | 0.4312(5) | 1.0708(3) | 0.1688(5) | 0.0153(6) | 0.0058(3) | 0.0198(6) | -0.0011(7) | -0.0151(1) | 0.0047(7) |
| N(1B) | 0.4829(4) | 0.4493(3) | 0.3590(3) | 0.0092(4) | 0.0038(3) | 0.0038(3) | -0.0004(5) | -0.0008(5) | -0.0012(4) |
| N(2B) | 0.4826(4) | 0.4553(3) | 0.1593(3) | 0.0079(4) | 0.0051(3) | 0.0041(3) | 0.0001(5) | -0.0007(5) | -0.0035(4) |
| N(3B) | 0.5019(4) | 0.8871(3) | 0.4194(3) | 0.0101(5) | 0.0044(3) | 0.0055(3) | -0.0021(6) | -0.0006(6) | -0.0047(5) |
| N(4B) | 0.5176(4) | 1.0228(3) | 0.2365(3) | 0.0076(4) | 0.0042(3) | 0.0071(3) | -0.0022(6) | -0.0010(6) | -0.0009(5) |
| C(1B) | 0.4873(4) | 0.5360(3) | 0.2427(3) | 0.0060(4) | 0.0041(3) | 0.0027(2) | -0.0003(5) | 0.0001(5) | -0.0014(4) |
| C(2B) | 0.6127(4) | 0.6148(3) | 0.2265(3) | 0.0044(4) | 0.0046(3) | 0.0035(3) | 0.0006(5) | 0.0003(5) | -0.0017(5) |
| C(3B) | 0.5781(4) | 0.6938(3) | 0.3109(3) | 0.0049(4) | 0.0038(3) | 0.0030(3) | -0.0007(5) | -0.0007(5) | -0.0010(4) |
| C(4B) | 0.6221(4) | 0.8189(3) | 0.2523(3) | 0.0048(4) | 0.0043(3) | 0.0039(3) | -0.0011(5) | -0.0005(5) | -0.0011(5) |
| C(5B) | 0.5066(4) | 0.8920(3) | 0.2904(3) | 0.0062(4) | 0.0036(3) | 0.0042(3) | -0.0019(6) | 0.0000(6) | -0.0007(5) |
| C(6B) | 0.3808(4) | 0.8343(3) | 0.2492(3) | 0.0043(4) | 0.0039(3) | 0.0041(3) | -0.0005(5) | -0.0004(5) | -0.0006(5) |
| C(7B) | 0.4121(4) | 0.7045(3) | 0.3092(3) | 0.0047(4) | 0.0036(3) | 0.0030(3) | -0.0006(5) | 0.0011(5) | -0.0009(4) |
| C(8B) | 0.3708(4) | 0.6301(3) | 0.2241(3) | 0.0045(4) | 0.0042(3) | 0.0029(3) | -0.0004(5) | -0.0001(5) | -0.0012(4) |
| C(9B) | 0.5782(4) | 0.6987(4) | 0.1098(3) | 0.0053(4) | 0.0055(3) | 0.0029(3) | -0.0003(6) | 0.0010(5) | -0.0009(5) |
| C(10B) | 0.5839(4) | 0.8262(4) | 0.1256(3) | 0.0051(4) | 0.0049(3) | 0.0038(3) | -0.0014(6) | 0.0010(5) | 0.0004(5) |
| C(11B) | 0.4202(4) | 0.8358(3) | 0.1238(3) | 0.0052(4) | 0.0044(3) | 0.0037(3) | -0.0001(6) | -0.0014(5) | 0.0007(5) |
| C(12B) | 0.4143(4) | 0.7086(3) | 0.1081(3) | 0.0052(4) | 0.0052(3) | 0.0025(2) | -0.0007(6) | -0.0007(5) | -0.0007(4) |

(less than 3σ) could be observed. Reflections with $I < 2.58\sigma(I)$ were indicated as unobserved. The intensities were corrected for Lorentz and polarization effects but no absorption correction was applied.

Crystal Data:

| | **21** | **22** |
|---|---|---|
| Molecular formula/mass | $C_{12}H_{11}N_3O_6$/293.2 | $C_{12}H_{10}N_4O_8$/338.2 |
| Space group | monoclinic $P2_1/c$ | triclinic $P\bar{1}$ |
| Lattice parameters | $a$ = 8.203 (5) Å | $a$ = 9.566 (6) Å $\alpha$ = 76.75 (5)° |
| | $b$ = 11.969 (8) | $b$ = 11.708 (6) $\beta$ = 89.39 (5) |
| | $c$ = 12.323 (6) | $c$ = 11.853 (6) $\gamma$ = 88.15 (5) |
| | $\beta$ = 108.17 (4)° | |
| Cell volume ($Z$) | 1149.6 Å$^3$ (4) | 1295.8 Å$^3$ (4) |
| Calculated density | $\varrho_c$ = 1.69 gcm$^{-3}$ | $\varrho_c$ = 1.73 gcm$^{-3}$ |
| Linear absorption coefficient | $\mu$(Mo-$K_\alpha$) = 1.294 cm$^{-1}$ | $\mu$(Mo-$K_\alpha$) = 1.396 cm$^{-1}$ |
| Number of independent reflections measured | 3341 | 6300 |
| Number of unobserved reflections | 1115 | 2094 |
| Statistic of $E$ values | $\langle \lvert E \rvert \rangle$ = 0.794 | $\langle \lvert E \rvert \rangle$ = 0.789 |
| | $\langle \lvert E^2 \rvert \rangle$ = 1.0 | $\langle \lvert E^2 \rvert \rangle$ = 1.0 |
| | $\langle \lvert E^2 - 1 \rvert \rangle$ = 0.955 | $\langle \lvert E^2 - 1 \rvert \rangle$ = 0.973 |
| $R$ Value | 0.06 | 0.07 |

Table 6. Fractional coordinates and isotropic temperature factors with standard deviation for the hydrogen atoms of **22**

| Atom | x | y | z | B |
|---|---|---|---|---|
| H(2A) | 1.774(4) | 0.239(4) | 0.367(3) | 1.0(8) |
| H(3A) | 1.845(4) | 0.376(4) | 0.182(3) | 1.0(8) |
| H(4A) | 1.783(4) | 0.209(3) | 0.108(3) | 1.0(8) |
| H(6A) | 1.215(4) | 0.242(4) | 0.098(3) | 1.0(8) |
| H(7A) | 1.092(4) | 0.395(4) | 0.180(3) | 1.1(8) |
| H(8A) | 1.208(4) | 0.282(4) | 0.360(3) | 1.2(8) |
| H(9A) | 0.902(5) | 0.038(4) | 0.409(4) | 1.3(9) |
| H(10A) | 0.897(4) | 0.022(4) | 0.201(4) | 1.3(9) |
| H(11A) | 1.160(4) | 0.040(4) | 0.204(3) | 1.0(8) |
| H(12A) | 1.153(4) | 0.070(4) | 0.399(3) | 1.0(8) |
| H(2B) | 0.705(4) | 0.573(4) | 0.240(3) | 1.0(8) |
| H(3B) | 0.627(4) | 0.663(4) | 0.387(3) | 1.0(8) |
| H(4B) | 0.714(4) | 0.837(4) | 0.271(3) | 1.0(8) |
| H(6B) | 0.287(4) | 0.865(4) | 0.263(3) | 1.0(8) |
| H(7B) | 0.365(4) | 0.678(4) | 0.387(3) | 1.2(8) |
| H(8B) | 0.269(5) | 0.603(4) | 0.229(4) | 1.4(9) |
| H(9B) | 0.638(5) | 0.678(4) | 0.044(4) | 1.3(9) |
| H(10B) | 0.638(5) | 0.884(4) | 0.067(4) | 1.1(9) |
| H(11B) | 0.370(4) | 0.900(4) | 0.066(4) | 1.2(9) |
| H(12B) | 0.358(5) | 0.693(4) | 0.035(4) | 1.5(9) |

The structures were solved with direct phasing. The $E$-map clearly showed the non-hydrogen atoms (Tables 3 and 5). The hydrogen atoms could all be seen in difference Fourier syntheses (Tables 3 and 6). The structures were refined with block-diagonal least-squares calculations with the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and $w = 1$. Anisotropic temperature factors for the C, N, O atoms were applied, and with isotropic

temperature factors for the H atoms. The atomic scattering factors were taken from *Ibers* and *Hamilton*[31]. The final difference Fourier syntheses did not show any peak higher than $\pm 0.4$ *e*/Å. All calculations and drawings were accomplished using the KRIPROG program[32,33].

Table 7. Bond lengths and angles in **22** (molecule A only)

| A–B | (Å) | A–B | (Å) |
|---|---|---|---|
| C(1)–N(1) | 1.516(6) | C(7)–H(71) | 0.992(41) |
| C(1)–N(2) | 1.515(7) | C(7)–C(8) | 1.537(6) |
| C(1)–C(2) | 1.526(6) | C(8)–H(81) | 1.022(42) |
| C(1)–C(8) | 1.514(6) | C(8)–C(12) | 1.541(6) |
| C(2)–H(21) | 1.016(41) | C(9)–H(91) | 1.054(49) |
| C(2)–C(3) | 1.542(6) | C(9)–C(10) | 1.550(7) |
| C(2)–C(9) | 1.531(6) | C(9)–C(12) | 1.576(5) |
| C(3)–H(31) | 1.053(41) | C(10)–H(101) | 0.995(45) |
| C(3)–C(4) | 1.536(6) | C(10)–C(11) | 1.575(5) |
| C(3)–C(7) | 1.591(5) | C(11)–H(111) | 1.002(42) |
| C(4)–H(41) | 1.013(42) | C(11)–H(12) | 1.546(7) |
| C(4)–C(5) | 1.524(6) | C(12)–H(121) | 0.977(44) |
| C(4)–C(10) | 1.539(6) | N(1)–O(1) | 1.193(7) |
| C(5)–N(3) | 1.512(5) | N(1)–O(2) | 1.212(6) |
| C(5)–N(4) | 1.515(6) | N(2)–O(4) | 1.206(6) |
| C(5)–C(6) | 1.526(6) | N(2)–O(3) | 1.215(6) |
| C(6)–H(61) | 1.011(42) | N(3)–O(6) | 1.209(5) |
| C(6)–C(11) | 1.532(6) | N(3)–O(5) | 1.217(5) |
| C(6)–C(7) | 1.533(6) | N(4)–O(7) | 1.214(5) |
| | | N(4)–O(8) | 1.221(5) |

| A–B–C | (°) | A–B–C | (°) |
|---|---|---|---|
| C(8)–C(1)–N(2) | 113.0(4) | C(5)–C(6)–C(11) | 102.8(3) |
| C(8)–C(1)–N(1) | 115.6(3) | C(5)–C(6)–C(7) | 101.0(3) |
| C(6)–C(1)–C(2) | 98.4(3) | C(11)–C(6)–C(7) | 102.3(3) |
| N(2)–C(1)–N(1) | 103.1(3) | C(6)–C(7)–C(8) | 107.2(3) |
| N(2)–C(1)–C(2) | 115.0(3) | C(6)–C(7)–C(3) | 103.7(3) |
| N(1)–C(1)–C(2) | 112.3(3) | C(8)–C(7)–C(3) | 103.0(3) |
| C(1)–C(2)–C(9) | 102.5(3) | C(1)–C(8)–C(7) | 102.3(3) |
| C(1)–C(2)–C(3) | 101.1(3) | C(1)–C(8)–C(12) | 101.6(3) |
| C(9)–C(2)–C(3) | 102.0(3) | C(7)–C(8)–C(12) | 101.7(3) |
| C(4)–C(3)–C(2) | 107.2(3) | C(2)–C(9)–C(10) | 107.7(3) |
| C(4)–C(3)–C(7) | 103.0(3) | C(2)–C(9)–C(12) | 103.3(3) |
| C(2)–C(3)–C(7) | 103.7(3) | C(10)–C(9)–C(12) | 90.4(3) |
| C(5)–C(4)–C(3) | 101.8(3) | C(4)–C(10)–C(9) | 107.5(3) |
| C(5)–C(4)–C(10) | 102.0(3) | C(4)–C(10)–C(11) | 104.0(3) |
| C(3)–C(4)–C(10) | 101.9(3) | C(9)–C(10)–C(11) | 89.4(3) |
| N(3)–C(5)–N(4) | 101.5(3) | C(6)–C(11)–C(12) | 107.4(4) |
| N(3)–C(5)–C(4) | 116.1(3) | C(6)–C(11)–C(10) | 103.4(3) |
| N(3)–C(5)–C(6) | 112.7(3) | C(12)–C(11)–C(10) | 90.6(3) |
| N(4)–C(5)–C(4) | 113.4(3) | C(8)–C(12)–C(11) | 107.6(3) |
| N(4)–C(5)–C(6) | 116.1(3) | C(8)–C(12)–C(9) | 104.0(3) |
| C(4)–C(5)–C(6) | 98.0(3) | C(11)–C(12)–C(9) | 89.5(3) |

CAS Registry Numbers

**4**: 98230-16-1 / **5**: 98230-14-9 / **9**: 68297-12-1 / **10a**: 102402-92-6 / **10b**: 102402-94-8 / **11**: 102402-93-7 / **12**: 102427-33-8 / **13**: 104946-30-7 / **14**: 104946-31-8 / **15**: 105016-82-8 / **16**: 105016-83-9 / **17**: 104946-32-9 / **20**: 104946-33-0 / **21**: 105016-84-0 / **22**: 104946-34-1 / dimethyl disulfide: 624-92-0 / ethylene glycol: 107-21-1

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