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PAGODANE - AN UNDECACYCLIC $C_{20}H_{20}$-POLYQUINANE

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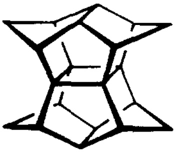
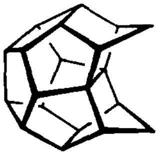
Pagodane, a highly symmetrical undecacyclic $C_{20}H_{20}$-polyquinane, is efficiently synthesized starting from "isodrin".

The highly symmetrical undecacyclic $C_{20}H_{20}$-hydrocarbon **1**, for which we propose the trivial name "pagodane" 1), is structurally closely related to its isomer dodecahedrane **3** 2), a relationship which might be used for the transformations **1** ⟶ **2** 3) ⟶ **3** 4).



1



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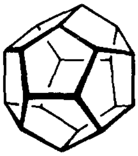

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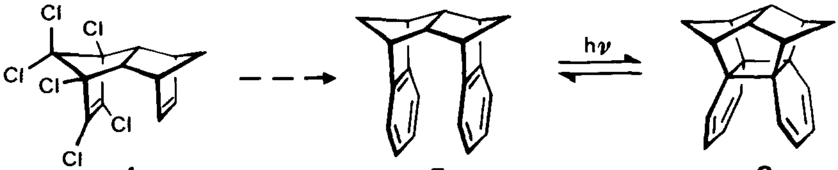
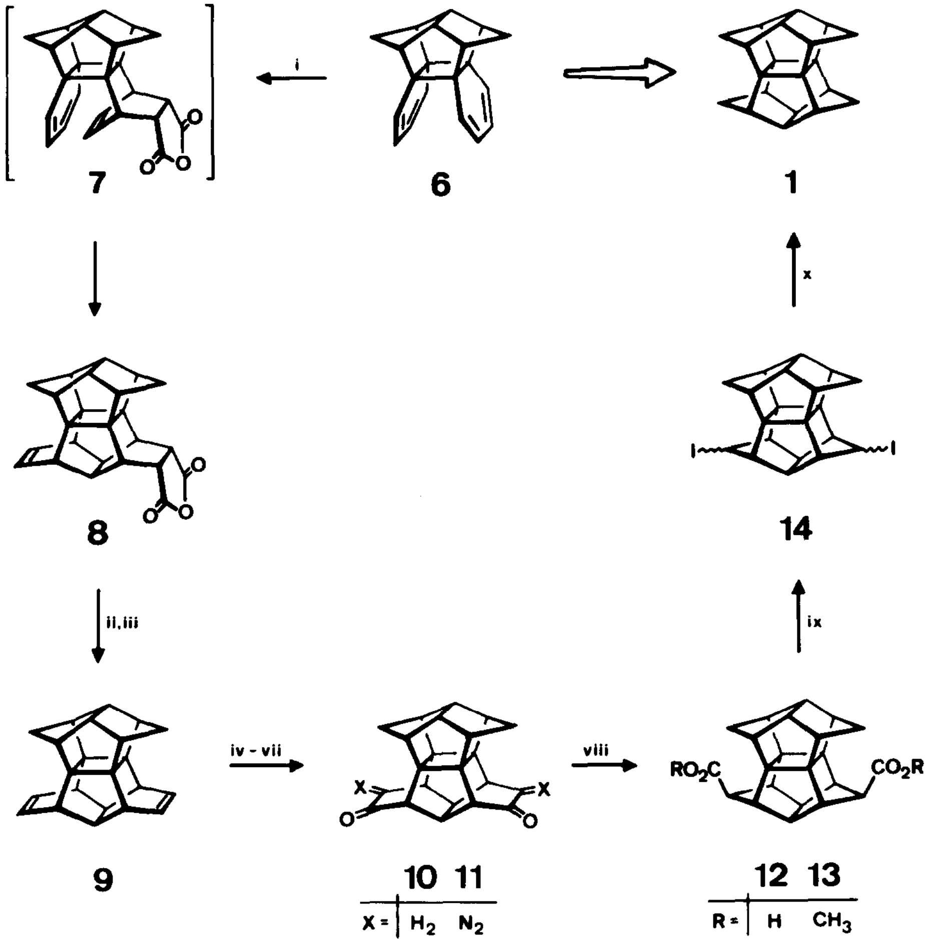
The synthesis of **1**, as outlined in the Scheme, starts with the $C_{20}H_{20}$-tetraene **6**, which we have made available through [6+6]-photocycloaddition of the dibenzo-isomer **5** 5,6). The attraction of this approach is enhanced in that **5** is now produced in a five-step sequence based on the industrial chemical "isodrin" **4** 7) with an overall yield of 55%, and that the photoreaction exclusively yields **6** (30% transformation) 8).



4 **5** **6**

In **6** the two diene units are ideally oriented for a domino-Diels-Alder reaction. Indeed, in boiling benzene the thermally rather stable **6** [6)] quantitatively and stereospecifically adds one equivalent of maleic anhydride. Under these conditions no trace of the endo-[4+2]-adduct **7** could be found (^{1}H-NMR), as it is quickly transformed into **8** (mp 184°C) [9)]. In the degradation of the corresponding diacid to the C_{2v}-diene **9** (mp 205°C) a reproducible 70% yield is achieved with Cu(I)oxide [10)] (30% with Pb(IV)tetraacetate). The ring contrac-

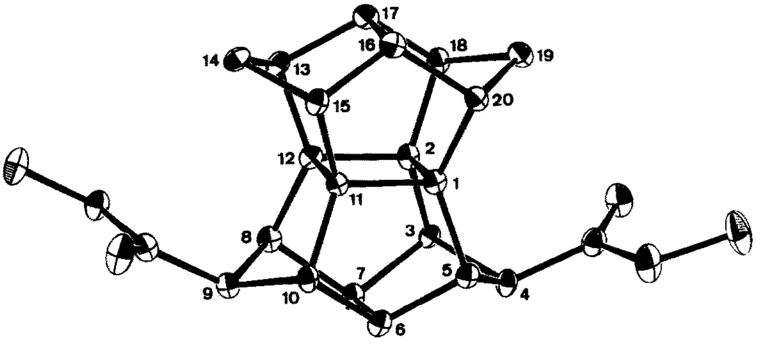
Scheme



(i) maleic anhydride/benzene, refl., 5h; (ii) KOH/methanol, refl., 10h; (iii) Cu_2O/2,2'-dipyridyl/quinoline, 180°C, 36h; (iv) BH_3/THF, 0°-20°C, 4h; NaOH/H_2O_2; (v) CrO_3/pyridine/CH_2Cl_2, 20°C, 1h; (vi) $HCOOCH_3$/NaH/THF, 20°C, 48h; (vii) $TosN_3$/NEt_3/THF, 20°C, 2h; (viii) THF/H_2O, 0°C, Vycor, high-pressure Hg-lamp; (ix) $Pb(OAc)_4/I_2/CCl_4$, refl., hν; (x) Na-K/THF/tert.-butanol, 20°C, 12h.

tions are performed using standard procedures: after hydroboration, oxidation (two isomeric diketones, e.g. **10**, 92%), formylation (80%) and diazotization (65%) [11], the bis-diazoketones (e.g. **11**) are photolysed in THF/water or dry methanol. Within the analytical limits (3%) only the endo,endo-diacid **12** (90% isolated) or the endo,endo-diester **13** (95% isolated, mp 269°C) are observed. Bis-iododecarboxylation [12] of **12** gives the isomeric diiodides **14** (80%), which are quantitatively reduced to **1** (mp 243°C, m/e = 260 (M^+, 100%)). The D_{2h}-symmetry is manifested by the simplicity of the ^1H- and ^{13}C-NMR spectra ($CDCl_3$): δ = 1.58 (AB, 8H), 2.24 (m, 8H), 2.60 (m,4H); δ = 62.9 (s, 4C), 59.6 (d, 4C), 42.7 (d, 8C), 41.9 (t, 4C).

From consideration of molecular models and from empirical force field calculations [13], it emerges that the strain inherent in the pagodane molecule should cause appreciable lengthening of the C6-C7 (C16-C17) and C1-C2 (C11-C12) bonds, the latter being the ones to be broken on the way to **3** [14]. The X-ray analysis of the diester **13** (Fig.) [15] provides pertinent data and also



<u>Fig</u>. Molecular structure of **13**. Selected bond lengths:

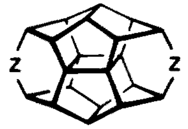
C6-C7 (C16-C17) : 1.617(6) (1.625(6)) Å

C1-C2 (C11-C12) : 1.585(5) (1.593(5)) Å

C1-C11 (C2 -C12) : 1.548(5) (1.555(5)) Å

confirms the endo position of the substituents. The prerequisites are thus given for the synthesis of bridged derivatives e.g. of type **15**.

12 – – →



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1) Undecacyclo$[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]$ eicosan.

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4) For different approaches see: P.E. Eaton, Tetrahedron 35, 2189 (1979), cit. lit.; P. Deslongchamps and P. Soucy, ibid. 37, 4385 (1981); W.P. Roberts and G. Shoham, Tetrahedron Lett. 22, 4895 (1981); M.A. McKervey, P. Vibuljan, G. Ferguson and P.Y. Siew, J. Chem. Soc., Chem. Commun. 1981, 912; J.E. Baldwin and P.L.M. Beckwith, ibid. 1983, 279; G. Mehta and M.S. Nair, ibid. 1983, 439.

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9) The new compounds are characterized by elemental analysis and spectra (IR, MS, NMR).

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13) N.L. Allinger, J. Am. Chem. Soc. 99, 8127 (1977). We thank Dr. H.-D. Beckhaus for advice in using the QCPE Program No. 395.

14) Hydrogenolysis of the very long C6-C7/C16-C17 bonds in **1** would lead to a "bis"-[4]peristylane; see L.A. Paquette, A.R. Browne, C.W. Doecke and R.V. Williams, J. Am. Chem. Soc. 105, 4113 (1983).

15) Crystals are monoclinic, space group $P_{2_1}/_{c}$, a = 17.251, b = 6.073, c = 16.512 Å, $\beta = 92.24^{\circ}$, Z = 4. Number of reflections used in least squares refinements: 2327. Final R-factor: 0.062 .

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