products consisting of practically pure amino alcohols 4 (X = NEt_2) (0.39 g, 95% yield) and 6 (0.38 g, 93% yield), respectively (IR, ^1H NMR, and GC).

Reaction of Amino Alcohol 16 with $COCl_2$. A solution of amino alcohol 16 (0.050 g, 0.24 mmol) and pyridine (0.2 mL) in anhydrous benzene (6 mL) was treated at 0 °C with 5.4 M $COCl_2$ solution in benzene (0.6 mL), and the reaction mixture was left 20 min at 0 °C and then 10 min at rt. CH_2Cl_2 (20 mL) was added; evaporation of the washed (water, 10% aqueous HCl, saturated aqueous $NaHCO_3$, and water) organic solvent solution afforded a solid reaction product (0.057 g, 93% yield) consisting of 17, which was recrystallized from hexane/CH_2Cl_2 to give pure **(1β,4β,6α)-4-(benzyloxy)-8-oxo-7-oxa-9-azabicyclo[4.3.0]nonane (17)** (0.045 g, 76% yield) as a solid, mp 156–157 °C: IR, 5.81 μm; ^1H NMR δ 7.26–7.40 (m, 5 H, aromatic protons), 5.24 (br s, 1 H, NH), 4.56 and 4.48 (AB dd, 2 H, J = 12.2 Hz, OCH_AH_BPh), 4.39 (ddd, 1 H, $J_{b,e}$ = 3.8, $J_{b,c}$ = 11.2, and $J_{b,d}$ = 12.5 Hz, $W_{1/2}$ = 28.0 Hz, H_b), 3.93 (m, five lines, J = 2.8 Hz, $W_{1/2}$ = 6.7 Hz, H_a), 3.35 (ddd, 1 H, $J_{c,f}$ = 4.4 and $J_{c,g}$ = $J_{c,b}$ = 11.2 Hz, $W_{1/2}$ = 28.0 Hz, H_c). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.92; N, 5.66. Found: C, 67.85; H, 6.79; N, 5.44.

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Registry No. 1, 84029-18-5; 2, 84049-33-2; 3 (X = NEt_2), 136667-62-4; 3 (X = NEt_2)·HCl, 136667-63-5; 3 (X = NHBu-*t*), 136667-64-6; 4 (X = NEt_2), 136667-65-7; 4 (X = NEt_2)·HCl, 136667-66-8; 4 (X = NHBu-*t*), 136667-67-9; 5, 136667-68-0; 5·HCl, 136667-69-1; 6, 136667-70-4; 6·HCl, 136667-71-5; 7, 136667-72-6; 8, 136667-73-7; 9, 136667-74-8; 10, 136667-75-9; 14, 136667-76-0; 15, 136667-77-1; 16, 136667-78-2; 17, 136667-79-3; *t*-$BuNH_2$, 75-64-9; diethylamine, 109-89-7.

"Roofed" Polyquinanes: Synthesis and Electronic Structure

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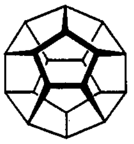
Starting from readily available norbornenobenzoquinone 7 and employing a photothermal metathesis reaction as the main strategy, novel "roofed" polyquinane bisenones 3 and 13 have been synthesized. Among these, the former is potentially serviceable for further elaboration to dodecahedrane 1. Catalytic hydrogenation of 3 provided the dione 12, which fully inscribes the circumference of dodecahedrane sphere. The "roofed" C_{16}-bisenone 3 has been successfully annulated to C_{19}-bisenone 24 and C_{19}-trisenone 26 by employing the Greene methodology and Pauson–Khand reaction, respectively. The molecular structures of 3 and 13 were computed using molecular mechanics and semiempirical MO methods. The nonbonded distances between the double bonds vary strongly with the method employed. The interactions between the π MO's were, therefore, probed by means of photoelectron (PE) spectroscopy. Comparison with the PE spectra of a series of model systems with increasing complexity enabled an unambiguous assignment of the observed peaks. The symmetric and antisymmetric combinations of the π MO's of the enone moieties of 3 and 13 show large splittings, characteristic of propano-bridged systems in which through-space and through-bond effects act in concert.

Introduction

Together with our travails in quest of dodecahedrane 1, through a "molecular stitching" approach,[1] we also ventured to explore an alternate convergent strategy to this enchanting hydrocarbon.[2] The convergent approaches to polycyclic molecules of high symmetry are considered aesthetically pleasing, shorter, and more attractive in total synthesis but are always difficult to execute due to variety of factors. In the case of dodecahedrane 1, the convergent approaches like the dimerization of triquinacene (C_{10} + C_{10}) initiated by Woodward,[3] capping of [5]peristylane (C_{15} + C_5) pursued by Eaton,[4] Paquette's bivalvane approach,[5] and Farnum's hexaene reorganization (C_8 + C_8 + C_4)[6] have all remained unattained despite their conceptual elegance. In spite of the failures of others, we considered a novel tetraquinane + diquinane (C_{12} + C_8) 2 approach to dodecahedrane 1 and sought to overcome the unfavorable steric and entropic factors, inherent in such approaches, taking recourse to a new tactic.



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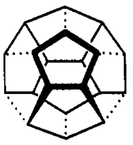

2

As the major impediment in the success of earlier convergent approaches to dodecahedrane has been the singular inability to properly align the two "halves" or "fragments"

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§ Department of Organic Chemistry, Indian Institute of Science.

[1] (a) Mehta, G.; Nair, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 7519. (b) Nair, M. S. Ph.D. Thesis, University of Hyderabad, 1984. (c) Mehta, G.; Reddy, K. R. *Tetrahedron Lett.* **1988**, *29*, 3607. (d) Mehta, G.; Reddy, K. R.; Nair, M. S. *Proc. Indian Acad. Sci.* (*Chem. Sci.*) **1988**, *100*, 223. (e) Mehta, G.; Nair, M. S.; Reddy, K. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1297.

[2] Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (b) Paquette, L. A. *Chem. Rev.* **1989**, *89*, 1051. (c) Fessner, W.-D.; Murthy, B. A. R. C.; Worth, J.; Hunkler, D.; Fritz, H.; Prinzbach, H.; Roth, W. D.; Schleyer, P. v. R.; McEwen, A. B.; Maier, W. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 452.

[3] Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162.

[4] Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

[5] Paquette, L. A.; Itoh, I.; Lipkowitz, K. B. *J. Org. Chem.* **1976**, *41*, 3524.

[6] Farnum, D. G.; Monego, T. *Tetrahedron Lett.* **1983**, *24*, 1361.

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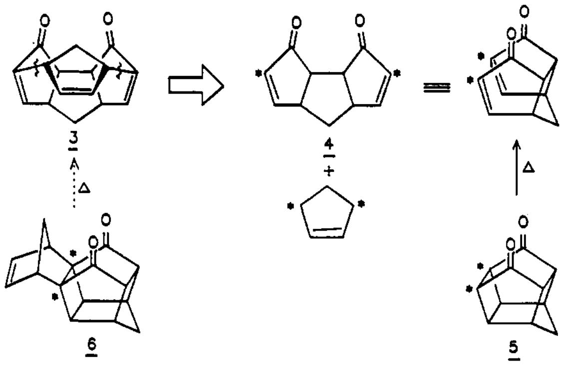
Scheme I



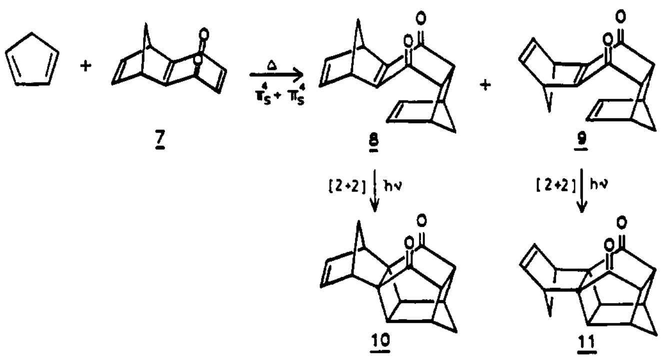
for installing the interconnecting C-C bonds, we decided to employ a strategy in which an advanced precursor to 1 could be obtained by uncaging a caged structure with the two halves already prealigned. Such a precursor was also expected to be endowed with adequate functionalization, carbon content, and carbocyclic rings to be amenable to evolution to 1. Retrosynthetic analysis of 1 through various bond disconnections, bearing in mind the convergent theme 2 led to a highly functionalized C_{16}-"roofed" polyquinane 3 as a very appealing advanced building block. As envisaged, 3 already has a prealigned cyclopentene ring in position which can be elaborated to the C_8 moiety of theme 2.

Our primary objective was, therefore, the design of a roofed polyquinane 3 and its further cyclopentannulation. In addition, the novel polyquinane 3 and its congeners also appeared to be of considerable interest in terms of their molecular and electronic structure. Besides the delineation of geometry of 3 by molecular mechanics and semiempirical MO methods, the nature of orbital interactions in it also deserved a scrutiny. The juxtaposition of three independent π units in 3 was expected to lead to strong through-space and through-bond interactions. In view of the current interest in obtaining a detailed understanding of the factors determining the relative strengths of such interactions in carefully chosen constrained systems,[7] we have obtained the photoelectron spectra of 3, as well as a series of related systems. The synthetic efforts leading to 3 and the results of PES studies and model MO calculations on it are detailed below.[8]

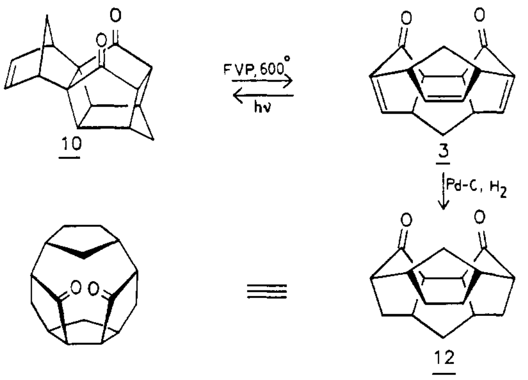
Synthetic Studies

The framework of 3 can be considered as composed of *cis,syn,cis*-triquinane bisenone 4 "roofed" by a bridged cyclopentene ring as shown (*) in Scheme I. This simple analysis showed a way to 3 as we have firmly established in earlier contributions from our laboratory,[9] a general and efficient route to triquinane bisenone 4 from the Cookson's caged dione 5 through thermally induced [2 + 2]-cycloreversion, Scheme I. Logically, this ready access to triquinane bisenone 4 could be extended to 3 by employing the appropriate precursor 6 having a 1,4-bridged cyclopentene (*), Scheme I. The heptacyclic caged dione precursor 6 can in turn be assembled along the lines of the synthesis of Cookson's caged dione 5.[10a]

Scheme II



Scheme III



Thus, Diels–Alder reaction between readily available norborneno-*p*-benzoquinone 7 and 1,3-cyclopentadiene furnished a diastereomeric mixture of *endo,syn*-8 and *endo,anti*-9 adducts (65:35) in high yield.[10] The predominant addition of cyclopentadiene to 7 from its "bottom side" to give *endo,syn*-8 has been rationalized by us in terms of steric effects.[11] Irradiation of 8 and 9 leads to intramolecular [2 + 2]-cycloadditions to furnish the caged heptacyclic diones 10 and 11 in 60–70% yield, Scheme II.[10] Of the two caged heptacyclic diones 10 and 11, the former has the correct stereochemical credentials for transformation to the desired C_{16}-"roofed" bisenone 3 through a [2 + 2]-cycloreversion process.

Sublimation of 10 through a quartz tube (flash vacuum pyrolysis, 600 °C/0.2 Torr)[9] resulted in a regioselective cyclobutane fragmentation, and the desired bisenone 3 was realized in 76% yield. The 9-line ^{13}C NMR spectrum with diagnostic signals at δ 207.1, 160.9, 153.6, and 135.5 fully supported this formulation. On irradiation by UV light 3 smoothly photocyclized back to the caged dione 10, Scheme III. On catalytic hydrogenation over Pd/C catalyst, roofed bisenone 3 furnished a hexahydro derivative 12 in 90% yield, Scheme III. The complete destruction of unsaturation in 12 was readily evident from its ^1H and ^{13}C NMR data. The dione 12 is a fascinating substrate and inscribes the complete circumference of the dodecahedrane sphere.

Having obtained the C_{16}-roofed triquinane bisenone 3, we also ventured to prepare and characterize the isomeric roofed polyquinane from the heptacyclic dione 11. On subjecting 11 to the FVP conditions the [2 + 2]-cycloreversion product 13 was realized in 50% yield and showed

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[7] Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369 and references cited therein.

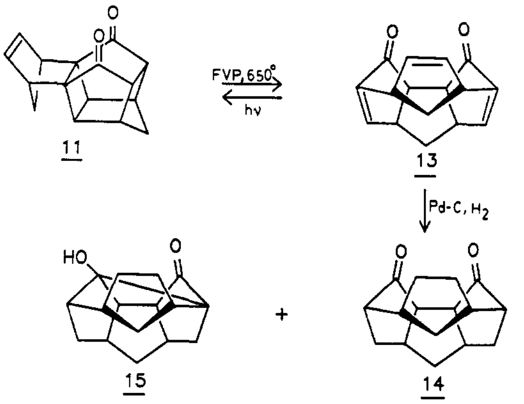
[8] Portions of the synthetic work have appeared in a preliminary communication: Mehta, G.; Reddy, K. R. *Tetrahedron Lett.* **1988**, *29*, 5309.

[9] (a) Mehta, G.; Reddy, A. V.; Srikrishna, A. *Tetrahedron Lett.* **1979**, 4863. (b) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.

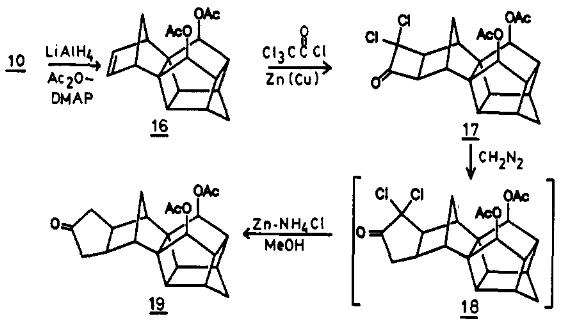
[10] (a) Cookson, R. C.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3043. (b) Mehta, G.; Padma, S. *J. Am. Chem. Soc.* **1987**, *109*, 7230. (c) Mehta, G.; Padma, S.; Karra, S. R.; Gopidas, K. R.; Cyr, D. R.; Das, P. K.; Geroge, M. V. *J. Org. Chem.* **1989**, *54*, 1342.

[11] Mehta, G.; Padma, S.; Pattabhi, V.; Pramanik, A.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2942.

Scheme IV



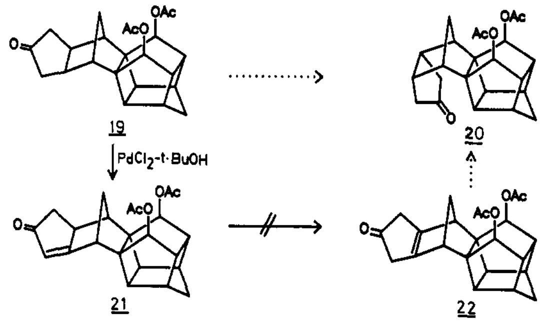
Scheme V



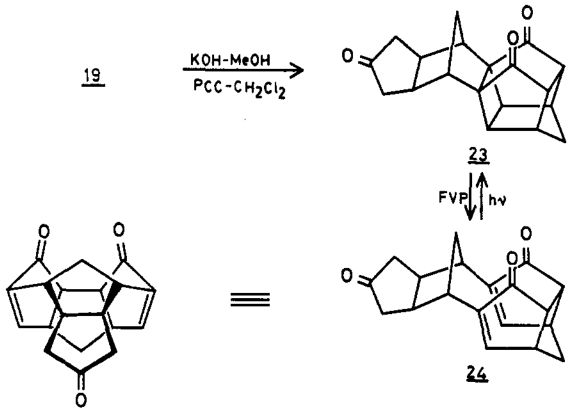
two sets of olefinic protons in the ^{1}H NMR spectrum at δ 6.74 (br s, 2 H) and δ 6.28 (s, 2 H) due to the presence of cyclopentenone and cyclopentene moieties, respectively. The ^{13}C NMR spectrum confirmed the existence of mirror plane symmetry and the diagnostic structural features with signals at δ 207.1, 158.6, 153.8, and 134.9. An unambiguous proof of bisenone structure **13** was obtained by its facile photocyclization to the caged precursor **11** (Scheme IV). Catalytic reduction of **13** over Pd/C catalyst led to a 1:1 mixture of saturated dione **14** and its internal aldol product **15**.

Construction of the C_8-diquinane (bicyclo[3.3.0]octane) moiety over the triquinane framework as envisaged in **2** was now attempted. This could be achieved most directly through the cyclopentannulation of the C_{16}-roofed polyquinene **3** already in hand. Since cyclopentannulation with regioselective placement of the carbonyl group was the desired objective, the Greene cyclopentannulation methodology[12] appeared to be the method of choice. However, reaction of **3** with dichloro ketene under a variety of conditions did not lead to the desired [2 + 2]-adduct.[13] Recognizing that the presence of two reactive bisenone moieties in **3** were perhaps complicating the dichloroketene addition, it was decided to go back a step to **10**, having a norbornene-type double bond. The only matter of concern was the presence of carbonyl groups in **10**, as it is known that the strained carbonyl groups react with dichloroketene to furnish β-lactones.[14] In order to preempt this possibility, the dione functionality in **10** was transformed to the diacetate **16** via LAH reduction and acetylation, Scheme V. Addition of excess of dichloroketene to the diacetate **16** furnished a 1:1 adduct **17** (85%). Exposure of **17** to diazomethane led to ring expansion to an unstable α,α'-dichlorocyclopentanone derivative **18**, which was directly dehalogenated with a Zn–NH$_4$Cl–MeOH recipe[12,15] to the

Scheme VI



Scheme VII



octacyclic keto diacetate **19** in 57% yield from **17**, Scheme V. The symmetry and structure of **19** was clearly indicated by its 13-line ^{13}C NMR spectrum with diagnostic cyclopentanone absorption at δ 220.6. The newly appended cyclopentanone ring in **19** has been assigned an exo stereochemical disposition based on the well-established propensity of norbornene double bond to undergo addition from its *exo* face.

Although the desired cyclopentanone annulation was conveniently accomplished, it was necessary to invert the stereochemistry of the newly appended ring as in **20** in order to correctly project the C_8-diquinane moiety on the triquinane framework for the "net-working" (see **2**) operation. To invert the norbornane ring junction in exo annulated **19**, it was planned to dehydrogenate it to the α,β-unsaturated enone **21** followed by isomerization of the double bond to bridgehead position as in **22** and stereoselective hydrogenation from the *exo* face to deliver the endo isomer **20**, Scheme VI. Toward this end, **19** was subjected to direct dehydrogenation employing Mincionne's[16] reaction conditions (PdCl$_2$ in *tert*-butyl alcohol) to furnish the desired enone–diacetate **21**. The next step toward the inversion maneuvre was the deconjugation of the α,β-unsaturated enone **21** to the β,γ-isomer **22**, and it was decided to effect this through a variety of methods like ketalization, equilibration with base and acid, etc., but none of them promoted the double bond isomerization in **21**. We, therefore, postponed ring inversion manuvre and decided to forge ahead with keto diacetate **19**, which had to be prepared for the thermal [2 + 2]-cycloreversion process.

The two acetate groups in **19** were first transformed to the carbonyl groups via hydrolysis with methanolic KOH and oxidation with PCC, Scheme VII. The resulting

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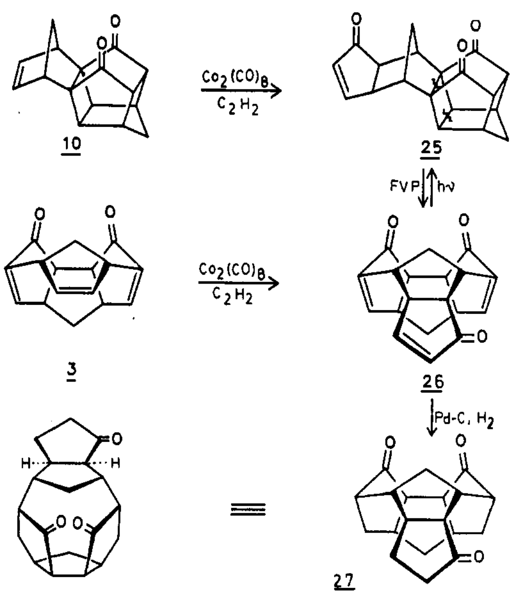
[12] Greene, A. E.; Depres, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 4003.
[13] Mehta, G.; Rao, H. S. P. *Synth. Commun.* **1985**, *15*, 991.
[14] Mehta, G.; Nair, M. S. *Ind. J. Chem.* **1988**, *27B*, 701.
[15] Noyori, R.; Balia, Y.; Hayakawa, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3336.
[16] Mincionne, E.; Ortaggi, G.; Sirna, A. *Synthesis* **1977**, 773.

Scheme VIII

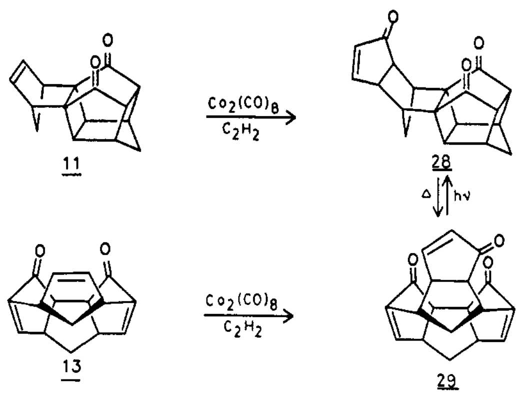


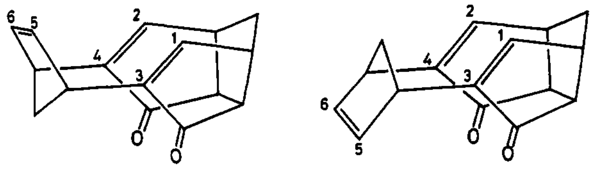
heptacyclic trione **23** was subjected to FVP conditions[9] to furnish C_{19}-bisenone **24** in 25% yield, Scheme VII. The ^{13}C NMR spectrum of **24** had carbonyl resonances at δ 219.0 and 208.1 (2 C), which ensured that all the three carbonyl groups of **23** had survived the FVP conditions. As expected, **24** on irradiation reverted to the octacyclic trione **23**.

While the C_{19}-bisenone **24** representing union of C_{11} and C_8 polyquinane units was successfully arrived at, it was still not amenable to the inversion of the cyclopentanone ring, and many attempts in this direction once again remained unrewarded. At this stage, the possibility of directly annulating the heptacyclic dione **10** without taking recourse to the wasteful carbonyl masking and unmasking steps was considered, and the Pauson–Khand reaction[17] was chosen for this purpose despite the limitation that it would lead to an unsymmetrical annulation product.

Reaction of C_{16}-heptacyclic dione **10** with the acetylene complex of $Co_2(CO)_8$ led to the ene–trione **25** in 78% yield. The presence of the cyclopentenone moiety in **25** was quite apparent from the ^1H and ^{13}C NMR spectra, with the latter exhibiting carbonyl resonances at δ 211.4, 211.1, and 210.3. In analogy with the Pauson–Khand reaction of norbornene,[17] the newly appended cyclopentenone ring was assigned exo stereochemistry. Next, the caged ene–trione **25** was thermolyzed under FVP conditions[9] to the densely functionalized trisenone **26** in 78% yield. The emergence of two broad singlets at δ 6.76 and 6.80 in ^1H NMR spectrum and the presence of 9 sp^2 carbon resonances in the ^{13}C NMR spectrum confirm the formulation **26**. Quite remarkably, the trisenone **26** was not only obtained under FVP conditions but could be photocyclized back to the ene–trione **25** on exposure to UV light. The trisenone **26** could also be obtained directly by carrying the Pauson–Khand reaction on the C_{16}-bisenone **3** in 45% yield, Scheme VIII. Hydrogenation of **26** furnished a perhydro product **27**. Considering that **26** was still a very serviceable intermediate in pursuit of our theme, an attempt was made to invert the newly appended cyclopentenone ring in it. Consequently, **26** was exposed to a variety of acids, Lewis acids, bases, and thermal activation to relocate one of the enone moieties. However, success proved elusive in this case also.

Scheme IX





R (1,2)	2.76 , (3.20), [3.43]	2.78, (3.31), [3.50]
R (3,4)	2.69 , (3.01), [3.25]	2.69, (3.08), [3.26]
R (2,6)	2.89 , (2.97), [3.08]	3.73, (3.83), [3.89]
R (4,6)	2.48 , (2.52), [2.59]	2.47, (2.55), [2.60]

Figure 1. Selected nonbonded distances (Å) in **3** and **13** optimized at MM2, (MNDO), [MINDO/3] levels.

As compounds like the trisenone **26** are interesting in their own right, it was of interest to prepare this series of compounds from the stereoisomeric heptacyclic C_{16}-dione **11** also. Pauson–Khand reaction with **11** gave the cyclopentenone annulated product **28** in 60% yield. The C_{19}-ene–trione **28** of the syn series also underwent smooth [2 + 2]-cycloreversion on thermolysis under FVP conditions[9] to yield the trisenone **29** in 50% yield, Scheme IX. Structure of the trisenone **29** followed from its spectral data which exhibited close resemblance with the trisenone **26** of the anti series. The trisenone **29** could also be obtained directly from **13** via Pauson–Khand annulation but in low yield, Scheme IX. On irradiation with UV light **29** photocyclized to its precursor **28**.

Molecular and Electronic Structures of 3 and 13

Cage systems like **3** and **13** are highly interesting in terms of their structural features as well as orbital interactions involving different functional groups. We have, therefore, studied the geometric and electronic structural aspects by combined use of theory and experiment. The key geometric features of **3** and **13** viz., the nonbonded distances between the three π units, optimized by the molecular mechanics method (MM2)[18,19] differ substantially from those obtained from semiempirical MO theory (Figure 1). In the MM2 structures the two C=C fragments related by symmetry are separated by around 2.7 Å, but the gap increases to more than 3 Å at the MNDO level.[20] The geometries obtained with the MINDO/3 method[21] indicate an even larger distance between the nonbonded units. However, all the computed separations are well in the range in which [2 + 2]-cycloaddition is

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(17) (a) Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* 1977, *295*, 2. (b) Pauson, P. L. *Tetrahedron* 1985, *41*, 5855.

(18) Allinger, N. L. *J. Am. Chem. Soc.* 1977, *99*, 8127.

(19) Lalitha, S.; Chandrasekhar, J.; Mehta, G. *Tetrahedron Lett.* **1990**, *31*, 4219.

(20) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, *99*, 4899.

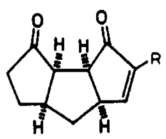
(21) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

Table I. Comparison between the Recorded Vertical Ionization Energies, $I_{v,j}$, of 3, 13, 30, and 34 with the Calculated Orbital Energies, ϵ_j (All Values in eV)

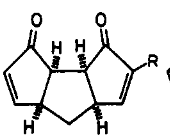
				$-\epsilon_j$	
compd	band	$I_{v,j}$	assignment	(MINDO/3)	(STO-3G)
30	1	8.8	n_-	9.27	8.02
	2	9.32	n_+	9.73	8.78
	3	9.9	π	10.19	8.21
31	1	8.85	n_-	9.22	8.21
	2	9.35	n_+	9.70	8.84
	3	9.70	π_-	10.08	7.94
	4	10.37	π_+	10.37	8.30
32	1	8.7	n_-	9.15	8.00
	2	8.7	π_-	9.70	7.37
	3	9.15	n_+	9.55	8.68
	4	9.8	π_+	10.09	7.90
33	1	8.47	π_-	9.65	6.99
	2	8.77	n_-	8.91	8.02
	3	9.14	n_+	9.45	8.70
	4	10.27	π_+	10.17	7.83
3	1	8.55	π_-	9.64	7.04
	2	8.85	n_-	8.92	8.08
	3	9.1	π_0	9.79	7.99
	4	9.52	n_+	9.30	10.06
	5	10.30	π_+	10.16	7.83
13	1	8.6	π_-	9.50	7.02
	2	8.8	π_0	9.85	7.62
	3	8.9	n_-	8.96	8.02
	4	9.48	n_+	9.20	8.73
	5	10.22	π_+	10.12	8.21
34	1	8.9	n_-		
	2	9.4	n_+		
	3	9.7	π		
35	1	8.7	n_-		
	2	9.2	n_+		
	3	9.3	π_-		
	4	10.2	π_+		

favored on purely geometric grounds (<4.2 Å) and hence are not in discord with the observed chemical behavior of these systems.[22] The relative position of the third C=C unit is roughly the same at all levels, the shortest contact being about 2.5 Å, in both **3** and **13**.

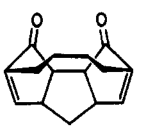
The orbital interactions involving the π units in **3** and **13** were quantified by He(I) photoelectron (PE) spectroscopy. The recorded vertical ionization energies $I_{v,j}$ of **3** and **13** together with the model compounds **30–35**[9] are collected in Table I. To assign the PE spectra we have employed an empirical approach by comparing the spectra of related systems, by using arguments from perturbation theory,[23] and also by using MO calculations in conjunction with Koopmans' theorem[24] as a guide.



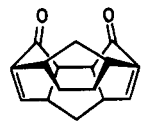
30, R=H
34, R=Me



31, R=H
35, R=Me



32



33

Let us consider the PE spectrum of **30**. It shows three distinct bands below 11 eV (see Figure 2). In comparison, the n-ionization of cyclopentanone is reported at 9.25 eV,[25] while for cyclopentenone the ionization energies are 9.34 eV (n) and 10.10 eV (π).[25] These data suggest that the first two bands of **30** at 8.8 and 9.32 eV should be assigned to ionization events from the two lone-pair combinations n_+ and n_-, as shown schematically in Figure 3. The third band in the PE spectrum of **30** (9.9 eV) is assigned to the π-MO of the cyclopentene unit. In line with this assignment is the observation that in the PE spectrum of **34** the third peak (π) is found at 9.7 eV while the first two bands in the PE spectrum of **34** remain nearly unchanged (Table I). In the PE spectrum of **31** we observe four bands below 11 eV. The correlation with those of **30** (see Figure 3) suggests that we assign the first two bands to the n_+ and n_- linear combinations.

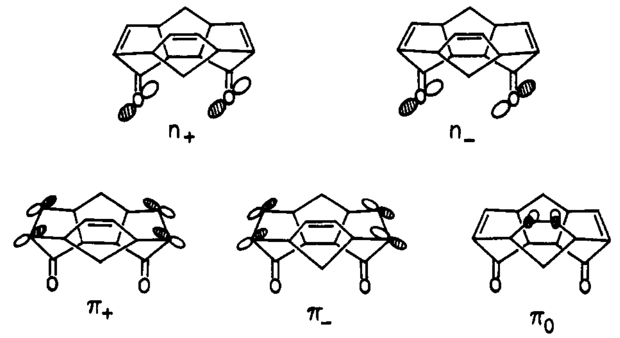


Figure 2. Schematic representation of key MO's of **3**.

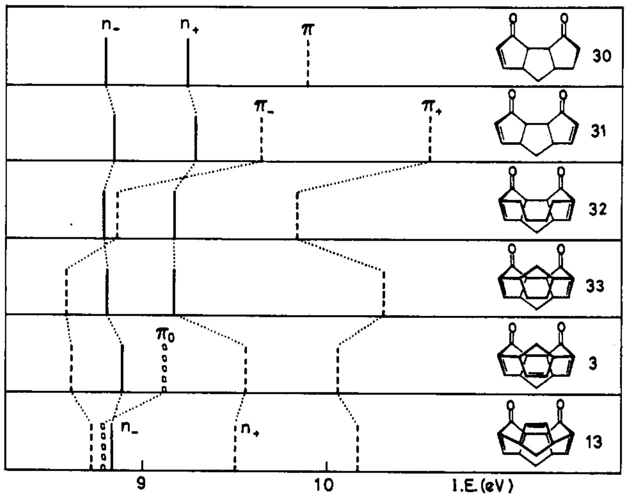


Figure 3. Assignment of the PE bands of **3**, **13**, **30–33**.

In addition, bands 3 and 4 are assigned to the two π linear combinations π_+ and π_- (see Figures 2 and 3). This assignment is confirmed by the comparison of bands 1–4 of **31** with those of **35**. Due to the alkyl substitution, only π_+ and π_- are shifted by 0.3 eV toward lower energy, while n_+ and n_- remain essentially constant (Table I). Comparing the PE spectrum of **31** with that of **32** we have to consider the inductive and hyperconjugative effects of the butano bridge on both π systems and the corresponding decrease of the distance between both π systems. All three effects explain the shift and the splitting of the π bands of **32** as compared to those of **31**. Model calculations (MM2) on **31** and **32** predict a distance between the π units of 3.21–3.51 Å for **31** and 2.86–2.90 Å for **32**. For **33** the mean distance between the nearly parallel enone units is considerably reduced (2.70 Å) as compared to **30–32**. Therefore, we expect a stronger splitting of the π bands in the PE spectrum of this compound. As can be seen from Figure 3, this expectation is met. The additional π bond in **3** and **13** should not affect the through-space interaction between the enone units very much, so we have assigned bands 1 and 5 in both PE spectra to ionization events from π_+ and π_-. To assign the π-MO of the bridging cyclo-

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pentene ring (π_0), we have considered two candidates in the PE spectrum of **3**: either band 4 (9.5 eV) or band 3 (9.1 eV). With the assignment of band 3, the split between n_+ and n_- in **3** and **13** remains essentially the same as in compound **30–33**. Furthermore, the ionization energy of π_0 also agrees with that of norbornene (8.97 eV).[26]

Orbital energies were also obtained for all six compounds using semiempirical (MINDO/3 and MNDO) and ab initio (STO-3G) MO methods. The results of the MINDO/3 and ab initio methods are listed in Table I. We find an agreement between the empirical assignment and the predicted MO sequence by MINDO/3 for **30** and **31**. In those cases where the peripheral enone rings are forced together by a bridge **3**, **13**, **32**, **33**, the splitting between π_+ and π_- is underestimated by the MINDO/3 procedure. This underestimation of through-space interaction has been documented for all NDDO methods.[27] The orbital energies computed by the ab initio method with the STO-3G basis set predicted the π-MO's at too low energy if we compare the results with our empirical assignment. In accord with our qualitative expectations, the calculations indicate that the n_+ and n_- linear combinations have roughly constant energies. The situation encountered in the interpretation of the PE spectra of **3**, **13**, **30–35**, namely that the calculated orbital energies disagree with an empirical assignment, is frequently encountered in enones[28] when n and π bands are close together.

The clearest feature in the above assignment of the PE spectra is the relatively large splitting between the symmetric and antisymmteric combinations of the π orbitals of the enone units. The principal reason for orbital splitting is, of course, the spatial proximity of the double bonds in **3** and **13**. But through-space interaction alone does not account for large differences in orbital energies. Many instances are known, even rigid systems with shorter separations between the double bonds,[7,29] in which through-bond interactions counteract the through-space effect. Detailed studies on a number of model systems have established that through bond effects via ethano bridges reverse the orbital ordering established by through-space interactions. On the other hand, through-bond interactions mediated by propano bridges enhance the splitting produced by through-space overlap.[7,30] In both **3** and **13**, the enone units are held together by propano bridges. The antisymmetric combination of the bonds of the propano fragment destabilizes the π–MO, leading to a large separation between π_+ and π_- orbitals (see Figure 3). The π orbital energy differences in **3** and **13** are thus among the largest characterized so far.

Summary

In short, we have conceived a new, convergent $C_{12} + C_8$ approach toward dodecahedrane and, in pursuit of it, synthesised the key "roofed" polyquinane **3** with the desired carbocyclic overlap of subunits, employing a photothermal metathesis strategy. Successful cyclopentannulation of **3** to hexacyclic C_{19}-bis- and -trisenone systems was achieved, but efforts to project the newly annulated five-membered ring within the polyquinane hemisphere for "net working" to **1** have not yet fructified. PES and MO studies on **3** and **13** and model compounds have revealed the nature of through-bond and through-space interactions present in these systems.

Experimental Section

For a general write up, see ref 11. All solvent extracts were washed with brine and dried over anhydrous sodium sulfate before concentration on a rotary evaporator under reduced pressure. The PE spectra were recorded with a Perkin-Elmer PS 18 instrument. The recording temperatures were as follows: **3**, **13**, 150 °C; **30**, **31**, **34**, **35**, 70 °C; **32**, **33**, 140 °C. The spectra were calibrated with Xe and Ar, and a resolution of 20 mV on the $^2P_{3/2}$ argon line was obtained.

anti-**10** and *syn*-heptacyclo[$10.2.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}$]hexadec-13-ene-3,10-dione (**11**) were prepared from norbornenobenzoquinone (**7**) and cyclopentadiene as described by us earlier[10c] and as shown in Scheme II.

***anti*-Pentacyclo[$9.2.1.1^{2,5}.1^{7,10}.0^{4,8}$]hexadeca-2(15),10(16),12-triene-3,9-dione (3).** Caged dione **10** (100 mg, 0.42 mmol) was slowly sublimed [130 °C (0.2 Torr)] through a quartz tube equilibrated to 600 °C (±10 °C) as described in the general procedure for FVP.[9] The condensate was carefully chromatographed over neutral alumina (15 g). Elution with 70% ethyl acetate–hexane gave starting dione **10** (15 mg, 15%) followed by bisenone **3** (65 mg, 65%), mp 222 °C, on crystallization from a mixture of CH_2Cl_2–hexane: IR ν_{max} (KBr) 3050, 2950, 1700, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.56 (s, 2 H, *H*C=CC=O), 6.44 (s, 2 H, *H*C=C*H*) 3.5–3.1 (m, 6 H), 3.0–1.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 207.1, 160.9, 153.6, 135.5, 55.6, 47.0, 40.7, 33.4, 32.0. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.56; H, 5.98.

***anti*-Pentacyclo[$9.2.1.1^{2,5}.1^{7,10}.0^{4,8}$]hexadecane-3,9-dione (12).** A solution of bisenone **3** (20 mg, 0.08 mmol) in 10 mL of ethyl acetate was hydrogenated over 10% Pd/C (5 mg) catalyst at 25 psi in a 250-mL Parr hydrogenation bottle for 2 h. The solution was filtered, and the filtrate was concentrated. The residue was charged over a silica gel (10 g) column and eluted with 50% ethyl acetate–hexane to furnish **12** (18 mg, 90%), mp 183 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1–1.0 (series of m, 20 H); ^{13}C NMR ($CDCl_3$) δ 223.2, 59.1, 49.2, 42.1, 39.8, 36.4, 33.4, 30.1, 29.4. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.64; H, 8.25. Found: C, 78.52; H, 8.29.

***syn*-Pentacyclo[$9.2.1.1^{2,5}.1^{7,10}.0^{4,8}$]hexadeca-2(15),10(16),12-triene-3,9-dione (13).** The syn photoadduct **11** (100 mg, 0.42 mmol) was sublimed at 150 °C (0.2 Torr) through a quartz tube, preheated to 650 °C (±10 °C).[9] The condensate deposited in the collection flask was chromatographed over a neutral alumina (15 g) column. Elution with 70% ethyl acetate–hexane gave the starting material **11** (20 mg, 20%) followed by **13** (40 mg, 40%), mp 252–253 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 3050, 2950, 1700, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.74 (s, 2 H, *H*C=CC=O), 6.28 (s, 2 H, *H*C=C*H*), 3.5–3.1 (m, 6 H), 2.64–1.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 207.1, 158.6, 153.8, 134.9, 55.9, 51.9, 48.1, 40.4, 31.0. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.69; H, 6.02.

Hydrogenation of 13. The bisenone **13** (20 mg, 0.08 mmol) was hydrogenated, and the crude product was purified as described for **12** to furnish **14** (7 mg, 35%): IR ν_{max} (KBr) 2925, 1730, 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.48–1.40 (series of m, 20 H); ^{13}C NMR ($CDCl_3$) δ 222.6, 58.5, 52.6, 46.0, 41.7, 41.1, 34.0, 32.1, 27.9. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.64; H, 8.25. Found: C, 78.37; H, 8.32. Continued elution with the same solvent system gave **15** (6 mg, 30%): IR ν_{max} (KBr) 3400, 2925, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.20–0.70 (series of m, 20 H). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.64; H, 8.25. Found: C, 78.43; H, 8.21.

***anti*-3,10-Diacetoxyheptacyclo[$10.2.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}$]hexadec-13-ene (16).** A solution of the caged dione **10** (240 mg, 1 mmol) in dry ether (25 mL) was added to a dispersion of LAH (40 mg, 1 mmol) in dry ether and stirred for 3 h. Quenching and extraction with ethyl acetate gave the diol (195 mg, 80%), mp 187–188 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 3200, 2950, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.4 (t, 2 H, C*H*=C*H*), 4.8–4.3 (m, 2 H), 3.92 (s, 2 H), 2.7–0.92 (series of m, 12 H). Anal.

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Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.12; H, 7.44. A mixture of diol (165 mg, 0.72 mmol), 4-(dimethylamino)pyridine (260 mg, 2.1 mmol), and acetic anhydride (0.3 mL, 0.3 mmol) in CH_2Cl_2 (40 mL) was stirred for 10 h. The crude product after the workup was chromatographed on silica gel (15 g). Elution with 50% ethyl acetate–hexane furnished the diacetate **16** (153 mg, 65%), mp 193 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1720, 1370, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.44–6.30 (m, 2 H, *H*C=C*H*), 4.96 (s, 2 H, C*H*OCOCH$_3$), 2.06 (s, 6 H, OCOC*H*$_3$), 3.1–1.0 (series of m, 12 H); ^{13}C NMR ($CDCl_3$) δ 170.9, 137.3, 72.1, 53.8, 50.6, 44.1, 43.1, 41.6, 40.9, 35.4, 21.4. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.48; H, 6.89.

13,16-*exo*-*anti*-3,10-Diacetoxy-15,15-dichlorooctacyclo$[10.4.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,16}]$octadecan-14-one (17). To a vigorously stirred mixture of the diacetate **16** (125 mg, 0.38 mmol) and Zn–Cu couple (250 mg, 3.8 mmol) in 300 mL of dry ether was added dropwise trichloroacetyl chloride (0.4 mL, 3.8 mmol) in 300 mL of dry ether over a period of 4 h. After stirring for 12 h at rt, the reaction mixture was filtered through a Celite pad, and the dark viscous residue was chromatographed on silica gel (20 g). Elution with 30% ethyl acetate–hexane furnished the dichloroketene adduct **17** (140 mg, 85%), mp 234 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2975, 1800, 1720, 1350 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.9–4.7 (m, 2 H, *H*COCOCH$_3$), 4.16–3.96 (m, 1 H, *H*CCOCCl$_2$), 3.48–3.3 (m, 1 H, COCCl$_2$C*H*), 2.76–1.0 (series of m, 12 H), 2.1 (s, 3 H, OCOC*H*$_3$), 2.06 (s, 3 H, OCOC*H*$_3$). Anal. Calcd for $C_{22}H_{22}O_5Cl_2$: C, 60.40; H, 5.07. Found: C, 60.82; H, 5.13.

13,17-*exo*-*anti*-3,10-Diacetoxyoctacyclo$[10.5.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$nonadecan-15-one (19). To a solution of **17** (100 mg, 0.2 mmol) in 50 mL of ether was added an excess of CH_2N_2 followed by 1 mL of methanol at 0–5 °C. After 45 min the ether was removed to furnish the crude product **18**. To a solution of this material in methanol (15 mL) was added NH_4Cl (110 mg, 2 mmol) and zinc powder (65 mg, 1 mmol) at 0 °C. The reaction mixture was brought to rt, stirred for 30 min, and filtered through a Celite pad. Methanol was removed under reduced pressure, and the residue was diluted with water and extracted with CH_2Cl_2 (25 mL × 3). The residue was charged on silica gel (15 g). Elution with 40% ethyl acetate–hexane furnished **19** (50 mg, 57%), mp 163 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1720, 1240, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.80 (br s, 2 H, *H*COCOCH$_3$), 2.04 (s, 6 H, OCOCH$_3$), 3.0–1.0 (series of m, 18 H); ^{13}C NMR ($CDCl_3$) δ 220.6, 171.0, 71.7, 53.5, 46.2, 43.7, 42.3, 41.9, 39.1, 38.9, 35.3, 33.3, 21.4. Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.22; H, 6.85. Found: C, 72.18; H, 6.86.

17-*exo*-*anti*-3,10-Diacetoxyoctacyclo$[10.5.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$nonadec-13(14)-en-15-one (21). To a solution of the diacetate **19** (25 mg, 0.06 mmol) in 10 mL of dry *tert*-butyl alcohol was added $PdCl_2$ (17 mg, 0.1 mmol), and the mixture was stirred at 90 °C for 3 h. The residue obtained after filtration through neutral alumina was chromatographed on silica gel (10 g). Elution with 50% ethyl acetate–hexane furnished enone **21** (18 mg, 72%), mp 173–174 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1720, 1700, 1620, 1300 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.90 (br s, 1 H, C=C*H*C=O), 4.92 (br s, 2 H, C*H*O), 3.4–3.1 (m, 2 H), 2.08 (s, 3 H, OCOC*H*$_3$), 2.06 (s, 3 H, OCOC*H*$_3$), 2.92–1.08 (series of m, 13 H); ^{13}C NMR ($CDCl_3$) δ 209.5, 192.6, 170.9 (2 C), 122.7, 72.06, 71.7, 56.1, 51.2, 48.0, 46.0, 45.8, 42.7, 42.6, 41.9 (2 C), 41.7, 41.6, 40.3, 39.0, 35.4, 21.4 (2 C). Anal. Calcd for $C_{23}H_{24}O_5$: C, 72.61; H, 6.35. Found: C, 72.53; H, 6.37.

13,17-*exo*-*anti*-Octacyclo$[10.5.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$nonadecane-3,10,15-trione (23). To a mixture of diacetate **19** (100 mg, 0.26 mmol), methanol (10 mL), and 1 mL of 10% aqueous KOH was stirred at rt for 6 h. Methanol was removed under reduced pressure, and the residue was diluted and extracted with CH_2Cl_2 (25 mL × 3) to furnish a diol (45 mg, 58%): IR ν_{max} (KBr) 3250, 2950, 1740, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.24–4.28 (m, 2 H, *H*COH), 3.76 (br s, 2 H), 3.2–0.9 (18 H, m). A solution of this diol (40 mg, 0.13 mmol) in 15 mL of dry CH_2Cl_2 was added to a solution of pyridinium chlorochromate (50 mg, 0.25 mmol) in 10 mL of CH_2Cl_2 containing activated molecular sieves (4 Å). After 30 min the contents were filtered through a Florosil pad and washed with ethyl acetate. Removal of solvent left a dark residue, which was charged on silica gel (15 g). Elution of the column with 80% ethyl acetate–hexane furnished the triketone **23** (28 mg, 74%), mp 226 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1740, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.4–1.1 (series of m, 18 H); ^{13}C NMR ($CDCl_3$) δ 219.5, 211.7, 61.8, 55.5, 44.1, 43.4, 42.6, 41.7, 38.3, 38.1, 35.4. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.41; H, 6.23.

3,7-*exo*-*anti*-Hexacyclo$[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]$nonadeca-1(17),9(18)-diene-5,10,16-trione (24). The triketone **23** (20 mg, 0.06 mmol) was sublimed at 190 °C (0.2 mm) through a quartz tube equilibrated to 630 °C (±10 °C).[8] The condensate was charged on a silica gel (10 g) column. Elution with ethyl acetate gave the unreacted starting material **23** (5 mg, 25%). Further elution furnished the bisenone **24** (5 mg, 25%), mp 240 °C, on crystallization from CH_2Cl_2–hexane, IR ν_{max} (KBr) 2900, 1730, 1700, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.76 (br s, 2 H, *H*C=CCO=O), 3.7–3.2 (m, 6 H), 3.1–1.2 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) δ 219.0, 208.1, 157.7, 154.0, 58.7, 47.5, 44.7, 44.5, 41.8, 31.4, 27.6; HRMS calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1260.

13,17-*exo*-*anti*-Octacyclo$[10.5.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$nonadec-15-ene-3,10,14-trione (25). The anti photoadduct **10** (480 mg, 2 mmol) was treated with $Co_2(CO)_8$ (685 mg, 2 mmol) in dry benzene (100 mL) at reflux for 3 h with acetylene and CO gently bubbled through the reaction simultaneously. The reaction mixture was filtered, concentrated, and charged over a silica gel (25 g) column. Elution with 80% ethyl acetate–hexane furnished **25** (458 mg, 78%), mp 249–250 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1720, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.68–7.4 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H, *H*C=CHC=O), 6.52–6.20 (d, J_1 = 6 Hz, 1 H, CH=C*H*C=O), 3.4–1.5 (series of m, 10 H), 1.5–1.2 (AB q, $J_1 = J_2$ = 12 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 211.4, 211.1, 210.3, 164.7, 138.0, 61.8, 61.2, 55.7, 55.6, 48.8, 46.4, 44.2, 44.1, 41.8, 38.7, 38.3, 38.2, 37.4, 34.0. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.00; H, 5.59.

3,7-*exo*-*anti*-Hexacyclo$[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]$nonadeca-1(17),5,9(18)-triene-4,10,16-trione (26). The C_{19}-enone **25** (100 mg, 0.34 mmol) was sublimed at 190 °C (0.2 Torr) through FVP column equilibrated to 630 °C (±10 °C). The condensate in the collection flask was chromatographed over a silica gel (15 g) column. Elution with ethyl acetate gave starting diketo enone **25** (18 mg, 18%) followed by the trisenone **26** (60 mg, 60%), mp 262–263 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 3050, 2900, 1700, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.74–7.58 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1 H, *H*C=CHC=O), 6.80 (br s, 1 H, *H*C=CC=O), 6.76 (br s, 1 H, *H*C=CC=O), 6.4–6.1 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H, HC=C*H*C=O), 4.1–3.9 (m, 1 H), 3.56–1.08 (series of m, 11 H); ^{13}C NMR ($CDCl_3$) δ 210.7, 207.7, 207.4, 165.9, 158.2 (2 C), 153.2, 152.6, 135.7, 58.7, 58.5, 53.0, 50.0, 47.4 (2 C), 39.9, 38.1, 31.2, 25.6. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.13; H, 5.63.

3,7-*exo*-*anti*-Hexacyclo$[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]$nondeca-1-(17),5,9(18)-triene-4,10,16-trione (26) Directly from 3. A mixture of bisenone **3** (50 mg, 0.2 mmol) and $Co_2(CO)_8$ (70 mg, 0.2 mmol) in 50 mL of dry benzene was reacted as described above to give **26** (27 mg, 45%), which was found to be identical with the compound obtained from the earlier experiment.

3,7-*exo*-*anti*-Hexacyclo$[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]$nonadecane-4,10,16-trione (27). The trisenone **26** (50 mg, 0.17 mmol) in ethyl acetate (15 mL) was hydrogenated over 10% Pd/C (5 mg) at 25 psi to furnish the perhydro compound **27** (45 mg, 90%), mp 264–265 °C, on crystallization from CH_2Cl_2–hexane, IR ν_{max} (KBr) 2900, 1740, 1470 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.2–1.0 (series of m, 22 H); ^{13}C NMR ($CDCl_3$) δ 221.7, 220.9, 220.2, 59.1, 58.7, 55.8, 49.0, 48.8, 45.7, 45.0, 42.1, 41.7, 40.3, 39.6, 39.3, 32.0, 31.2, 30.7, 28.7. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.31; H, 7.41.

13,17-*exo*-*syn*-Octacyclo$[10.5.1.1^{5,8}.0^{2,6}.0^{2,11}.0^{4,9}.0^{7,11}.0^{13,17}]$nonadec-15-ene-3,10,14-trione (28). The syn photoadduct **11** (240 mg, 1 mmol) in dry benzene (10 mL) was reacted with $Co_2(CO)_8$ (340 mg, 1 mmol) in the presence of acetylene and CO as described earlier. Passage through silica gel (25 g) in 60% ethyl acetate–hexane gave **28** (177 mg, 64%), mp 216–218 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr) 2950, 1720, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–7.4 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1 H, *H*C=CHC=O), 6.4–6.1 (d, J_1 = 6 Hz, 1 H, HC=C*H*C=O), 3.7–3.4 (m, 1 H), 3.1–1.1 (series of m, 13 H); ^{13}C NMR ($CDCl_3$) δ 211.8, 211.4, 210.9, 165.3, 137.8, 57.4, 56.4, 55.8, 55.7, 46.0, 43.5, 43.4, 43.1, 40.7, 40.4, 40.1, 39.3, 38.9, 30.0. Anal. Calcd for

$C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.57.

3,7-*exo*-*syn*-Hexacyclo[12.2.1.$1^{2,8}$.$1^{9,12}$.$0^{3,7}$.$0^{11,15}$]nonadeca-1(17),5,9(18)-triene-4,10,16-trione (29). The diketo enone **28** (50 mg, 0.17 mmol) was sublimed at 200 °C (0.2 Torr) through a quartz tube preheated to 650 °C (±10 °C).[8] Chromatography over silica gel (10 g) in ethyl acetate gave starting **28** (14 mg, 28%) followed by trisenone **29** (18 mg, 36%), mp 277–278 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr): 3050, 2950, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7–7.5 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1 H, *H*C=CHC=O), 6.9–6.7 (m, 2 H, *H*C=CC=O), 6.30–6.08 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H, HC=C*H*C=O), 4.7–4.4 (m, 1 H), 4.08 (d, J = 6 Hz, 1 H), 3.7–1.5 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) δ 212.7, 207.7 (2 C), 167.0, 59.3, 159.2, 151.6, 150.9, 134.7, 57.9, 57.0, 49.5, 47.0, 46.8, 45.6, 44.3, 40.4, 39.0, 28.9. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.29; H, 5.67.

3,7-*exo*-*syn*-Hexacyclo[12.2.1.$1^{2,8}$.$1^{9,12}$.$0^{3,7}$.$0^{11,15}$]nonadeca-1(17),5,9(18)-triene-4,10,16-trione (29) Directly from 13. The bisenone **13** (50 mg, 0.20 mmol) was reacted with $Co_2(CO)_8$ (70 mg, 0.20 mmol) as described above to furnish **33** (35 mg, 33%). This material was identical with the sample characterized in the previous experiment.

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Registry No. 1, 4493-23-6; **3**, 126984-41-6; **10**, 119364-65-7; **10** diol, 127277-46-7; **11**, 119364-64-6; **12**, 126984-42-7; **13**, 127062-56-0; **14**, 127062-57-1; **15**, 126984-43-8; **16**, 126984-44-9; **17**, 126984-45-0; **19**, 126984-46-1; **19** diol, 126984-49-4; **21**, 136911-85-8; **23**, 126984-47-2; **24**, 136983-99-8; **25**, 136911-86-9; **26**, 136911-87-0; **27**, 136911-88-1; **28**, 136984-00-4; **29**, 136984-01-5; **30**, 82253-87-0; **31**, 82217-29-6; **32**, 106092-82-4; **33**, 130563-14-3; **34**, 136911-89-2; **35**, 136911-90-5; Cl_3CCOCl, 76-02-8; C_2H_2, 74-86-2.

Synthesis and Properties of Substituted 1,6-Dioxapyrene Donors

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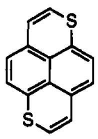
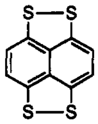
The synthesis of substituted 1,6-dioxapyrenes, **2b–g**, from 2,6-dipropyl-1,5-naphthalenediol (**7a**) or 2,6-dimethyl-1,5-naphthalenediol (**7b**) is described. Diol **7a** was prepared by Claisen allylic rearrangement followed by reduction, and **7b** was prepared by Mannich reaction of 1,5-naphthalenediol followed by base-promoted hydrogenolysis. The 1,6-dioxapyrenes can be oxidized to stable cation radicals at +0.2–0.35 V vs SCE and to dications at +0.8–1.20 V. The preparation of some tetracyanoquinodimethane salts and binary cation radical salts of the 1,6-dioxapyrenes is reported.

Introduction

Heterocyclic analogues of pyrenes are good electron donors. 1,6-Dithiapyrene[1] (**1**) has been demonstrated to give a highly conducting 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) salt.[2] Other 1,6-dithiapyrenes substituted with alkyl, aryl, alkoxy, or alkylthio substituents have similarly been found to form conducting molecular solids.[3,4] The 1,6-heteropyrenes are electronic equivalents of the donors dehydrotetrathianaphthazarin[5] (**1b**) and its selenium analogue.[6] We have been interested in studying the effect of oxygen in heterocyclic donor systems such as the 1,6–dioxapyrenes **2a–g** because oxygen is smaller and less polarizable than the sulfur and selenium heteroatoms. When 1,6–dioxapyrenes are used to generate conducting salts consisting of uniform stacks of molecules, we expect to obtain an increase in bandwidths as well as electronically more one-dimensional materials in comparison with the sulfur and selenium containing materials. The purpose of this work was to identify 1,6-dioxapyrenes capable of forming stoichiometric salts. In a second phase we intend to prepare the sulfur and selenium analogues of selected 1,6-dioxapyrenes and evaluate in detail the effects of the heteroatoms in an isostructural series of 1,6-dichalcogenpyrene based conducting materials. We report the preparation[7] six new alkyl and aryl derivatives, **2b–g**, of 1,6-dioxapyrene, and we have attempted to prepare the parent system. Very recently **2a** was prepared[8] by a procedure different from the general procedure presented here. The analogous oxaphenalene[9a] (**3a**) and thiaphenalene[9b] (**3b**) have been described previously. Several conducting solids based on other oxygen-containing donors have been pre-



1



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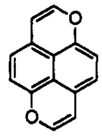

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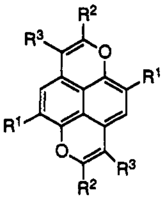
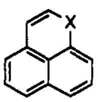


2b-g



3a, X=O
3b, X=S

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