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Acid and Base Promoted Rearrangements of Hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione

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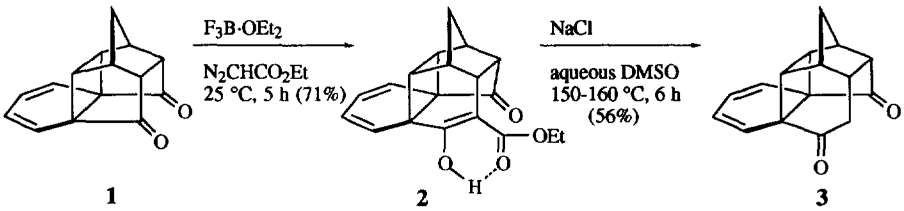
Abstract. Hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione (**3**) was synthesized via ring-expansion of hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (**1**). Reaction of a toluene solution of **3** with a catalytic amount of HCl resulted in extensive skeletal rearrangement, thereby affording 6,7-benzotetracyclo[7.3.0.0^{4,12}.0^{5,10}]dodecane-2,6-dione (**4**). Subsequent reaction of **4** with 3,6-diphenyl-1,2,4,5-tetrazine (**5**) afforded a novel molecular cleft, **6**. Compound **3** reacted smoothly with ethanolic KOH at ambient temperature (in 3 h) or at reflux (in 0.5 h) to afford a rearranged product, **7**. The structures of **3**, **4**, **5**, and **7** were established unequivocally via application of single crystal X-ray crystallographic methods. Copyright © 1996 Elsevier Science Ltd

Introduction. As part of an ongoing program which is involved with the synthesis and chemistry of novel polycarbocyclic "cage" compounds,[1] we recently reported procedures for performing Lewis acid-promoted ring-expansion reactions on substituted pentacyclo[5.4.0.0^{2,6}.0^{4,10}.0^{5,9}]undecane-8,11-diones with ethyl diazozcetate (EDA).[2] As an extension of this study, we now report the synthesis of hexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione (**3**, Scheme 1) via ring-expansion of hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione[3] (**1**, Scheme 1). In addition, we have studied acid and base promoted rearrangements of **3**, each of which proceeds with extensive skeletal rearrangement (*vide infra*).

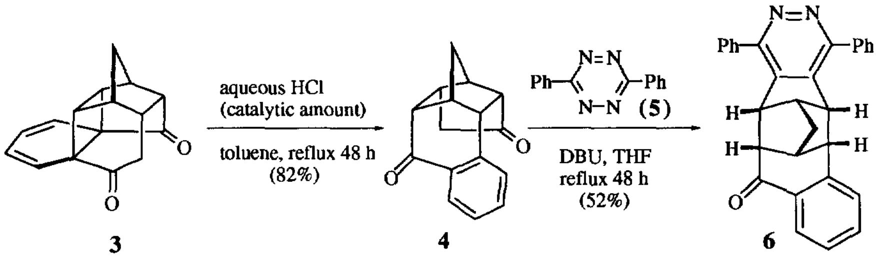
Results and Discussion. The procedure by which hexacyclic cage diketone **3** was synthesized via ring expansion of **1** is summarized in Scheme 1. Both of the reactions shown in Scheme 1 proceed smoothly and in good yield. Unequivocal verification of the structure of **3** was secured via application of X-ray crystallographic methods.

Next, the chemical behavior of **3** toward a protic acid and toward aqueous ethanolic KOH were explored. Thus, when a toluene solution of **3** which contains a catalytic amount of aqueous HCl is refluxed, extensive skeletal rearrangement of the carbocyclic cage framework occurs with concomitant formation of a new diketone, **4** (Scheme 2). The structure of **4** was established unequivocally via X-ray crystallographic analysis. In addition, **4** was reacted with 3,6-diphenyl-1,2,4,5-tetrazine[4] (**5**) to produce a molecular cleft[5] **6**, (Scheme 2), whose structure was established via X-ray crystallographic analysis.

Scheme 1

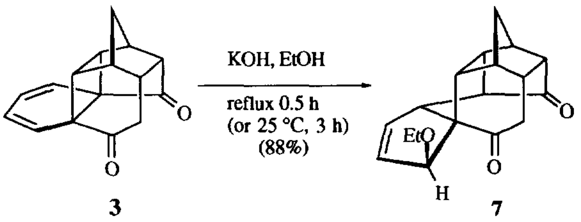


Scheme 2



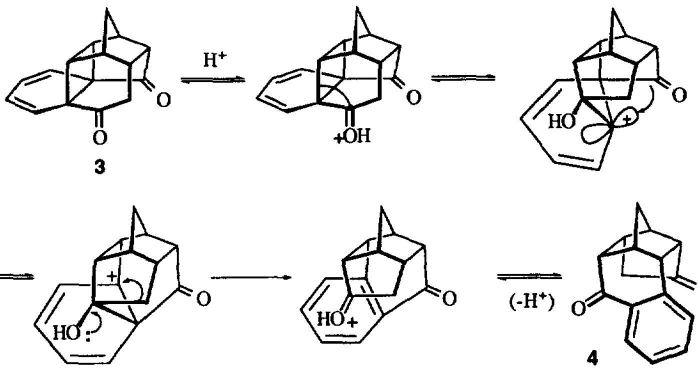
Finally, the reactivity of **3** toward base was explored. No reaction occurred when **3** was refluxed with aqueous base. However, **3** reacted smoothly with ethanolic KOH at ambient temperature (in 3 h) or at reflux (in 0.5 h) to afford a rearranged product, **7** (Scheme 3). The structure of **7** was established via X-ray crystallographic analysis.

Scheme 3



On the Mechanisms of the Acid and Base Promoted Rearrangements of 3. A plausible mechanism for the acid promoted rearrangement of **3** to **4** is presented in Scheme 4. The suggested mechanism finds precedent in the corresponding acid promoted rearrangement of **1** (Scheme 5), which has been reported to afford **8** and **9**, both of which are close structural analogs of **4**.[6] In addition, Baeyer-Villiger oxidation of **1**, performed in glacial acetic acid, also affords an extensively rearranged product, **10** (Scheme 5), which is a structural analog of **4**.[7]

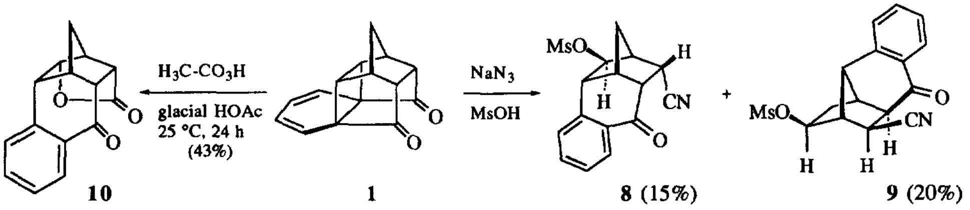
Scheme 4



3

4

Scheme 5



10

1

8 (15%)

9 (20%)

A corresponding mechanism which is forwarded to account for the base promoted rearrangement of **3** to **7** is shown in Scheme 6. The calculated heats of formation of two carbanionic intermediates (**11** and **12**) and their corresponding conjugate acids (**13** and **7**, respectively) are shown in Table 1. Interestingly, while rearrangement of anion **11** to anion **12** is predicted by the results of semi-empirical molecular orbital calculations[7] to be endothermic by *ca.* 6 kcal-mol^{-1}, their respective conjugate acids lie in the opposite order of relative stability (i. e., compound **7**, the observed product of base promoted rearrangement of **3**) is favored thermodynamically relative to **13** by *ca.* 18 kcal-mol^{-1}).

Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Phoenix, AZ.

3-Carboethoxyhexacyclo[11.2.1.0^{2,12}.0^{5,10}.0^{5,15}.0^{10,14}]hexadeca-6,8-diene-4,11-dione (2). tion of cage diketone **1**[3] (500 mg, 2.23 mmol) in Et_2O (10 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added sequentially with stirring $F_3B{\cdot}OEt_2$ (0.30 mL, 2.5 mmol) and ethyl diazoacetate (EDA, 0.31 mL, 3.0 mmol). After the addition of reagents had been completed, the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at that temperature for 5 h. Diethyl ether (25 mL) was added, and the resulting mixture was

Scheme 6

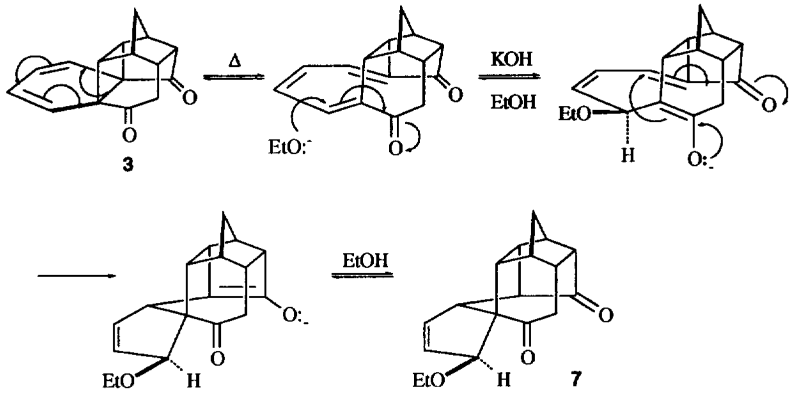
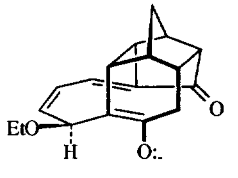
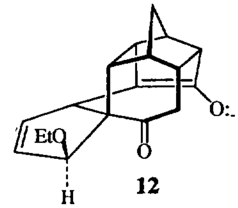
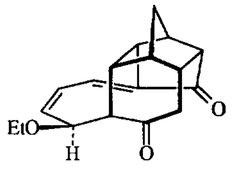
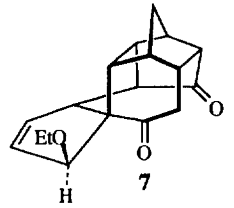


Table 1. Calculated heats of formation of **11**, **12**, **13**, and **7**

		
	11	**12**
ΔH_f (AM1, kcal-mol^{-1})	-84.07	-77.99
E_{rel} (kcal-mol^{-1})	(0)	(+6.07)
		
	13	**7**
ΔH_f (AM1, kcal-mol^{-1})	-63.91	-81.97
E_{rel} (kcal-mol^{-1})	(0)	(-18.05)

washed sequentially with water (2 x 25 mL), 10% aqueous $NaHCO_3$ (2 x 25 mL), and water (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 1:6 EtOAc-ligroin. Pure **2** (490 m g, 71%) was thereby obtained as a colorless microcrystalline solid, mp 145-146°C; IR ($CHCl_3$) 2906 (s), 1741 (s), 1656 (s), 1429 (w), 1309 (w), 1265 (m), 1091 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 8.1 Hz, 3 H), 1.42 (*A*B, J_{AB} = 10.8 Hz, 1 H), 1.80 (A*B*, J_{AB} = 10.8 Hz, 1 H), 2.26 (br s, 1 H), 2.7-3.1 (m, 4 H), 3.43-3.60 (m, 1 H), 4.08-4.35 (m, 2 H), 5.70 (d, J = 9.7 Hz, 1 H), 5.75 (d, J = 9.7 Hz, 1 H), 6.0-6.2 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.6 (q), 36.5 (t), 41.9 (d), 42,3 (d), 44.5 (s), 44.8 (d), 50.9 (d), 51.4 (d), 55.9 (d), 57.2 (s), 61.2 (t), 100.3 (s), 121.8 (d), 123.3 (d), 124.3 (2 C, d), 171.2 (s), 173.7 (s), 216.3 (s). Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.71; H, 5.65.

Hexacyclo[11.2.1.$0^{2,12}$.$0^{5,10}$.$0^{5,15}$.$0^{10,14}$]hexadeca-6,8-diene-4,11-dione (3).[9] A mixture of **2** (470 mg, 1.51 mmol), NaCl (300 mg, 5.13 mmol) and water (0.5 mL) in DMSO (10 mL) was heated at 150-160°C for 6 h. The reaction mixture was cooled to ambient temperature and then diluted with water (25 mL). The resulting aqueous suspension was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with water (2 x 25 mL), dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 1:5 EtOAc-ligroin. Pure **3** (200 mg, 56%) was thereby obtained as a colorless microcrystalline solid: mp 141-142 °C; IR ($CHCl_3$) 2968 (m), 1732 (vs), 1697 (vs), 1599 (w), 1392 (w), 1263 (w), 1161 (w) cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.41 (*A*B, J_{AB} = 10.2 Hz, 1 H), 2.62 (A*B*, J_{AB} = 10.2 Hz, 1 H), 2.32-2.80 (m, 6 H), 2.90 (br s, 1 H), 3.04-3.15 (m, 1 H), 5.32 (d, *J* = 10.3, 1 H), 5.45 (d, J = 10.3 Hz, 1 H), 5.80-6.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 38.2 (t), 39.2 (t), 40.1 (d), 41.3 (d), 45.2 (d), 48.4 (s), 50.0 (d), 52.4 (d), 53.6 (s), 54.0 (d), 121.5 (d), 123.2 (d), 124.5 (d), 126.1 (d), 208.9 (s), 218.6 (s). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.48; H, 5.77. The structure of **3** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Acid Promoted Rearrangement of 3. To a solution of **3** (200 mg, 0.84 mmol) in toluene (20 mL) was added concentrated aqueous HCl (2 drops, catalytic amount), and the resulting mixture was refluxed with stirring for 48 h. The progress of the reaction was monitored by thin layer chromatographic (tlc) analysis; the presence of **3** could no longer by detected by tlc analysis after 48 h. The reaction mixture was cooled to ambient temperature and then concentrated *in vacuo* . The residue was dissolved in Et_2O (20 mL), and the resulting solution was washed successively with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and water (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting with 15% EtOAc-hexane. Pure **4** (1.72 g, 82%) was thereby obtained as a colorless microcrystalline solid: mp 158-159 °C; IR ($CHCl_3$) 2960 (vs), 2874 (w), 1732 (vs), 1683 (vs), 1601 (s), 1456 (s), 1278 (s), 1147 (s), 833 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.61-2.21(m, 5 H), 2.73 (*A*B, J_{AB} = 11.3 Hz, 1 H), 3.00-3.06 (br s, 3 H), 3.45(A*B*, J_{AB} = 11.3 Hz, 1 H), 7.22 (d, *J* = 7.5 Hz, 1 H). 7.34 (d, *J* = 7.5 Hz, 1 H), 7.50 (*A*B, J_{AB} = 6.8 Hz, 1 H), 8.00 (A*B*, J_{AB} = 6.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.8 (t), 40.5 (d). 41.1 (t), 45.6 (d), 46.1 (d), 48.9 (d), 51.5 (d), 55.6 (d), 127.1 (d), 128.3 (d), 130.1 (d), 130.9 (s), 135.0 (d), 143.1 (s), 200.2 (s), 219.2 (s). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.76; H, 5.94. The structure of **4** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Diels-Alder Cycloaddition of 4 to 3,6-Diphenyl-1,2,4,5-tetrazine (5). To a refluxing solution of **4**[4] (290 mg, 1.26 mmol) and **5** (377 mg, 1.64 mmol) in dry THF (20 mL) was added DBU (0.48 mL, 3.2 mmol), and the resulting mixture was refluxed with stirring for 48 h. The reaction mixture was allowed to cool to ambient temperature and then concentrated *in vacuo*. Methanol (7 mL) was added to the residue, whereupon a colorless precipitate formed. The precipitate was collected via suction filtration, and the residue was washed with methanol (2 x 5 mL). The resulting solid was purified via recrystallization from EtOAc-hexane, thereby affording pure **6** (280 mg, 52%) as a colorless microcrystalline solid: mp 205.0-205.5 °C; IR ($CHCl_3$) 2961 (vs), 2881 (w), 1676 (vs), 1606 (m), 1460 (m), 1377 (s), 1298 (m), 1111 (m), 925 (m), 746 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.98 (*A*B, J_{AB} = 11.3 Hz, 1 H), 2.11 (A*B*, J_{AB} = 11.3 Hz, 1 H), 3.07-3.15 (m, 2 H), 3.33-3.42 (m, 1 H), 3.66-3.70 (m, 1 H), 3.82-3.87 (dd, *J* = 10.2, 3.8 Hz, 1 H), 3.98-4.04 (dd, *J* = 10.2, 3.8 Hz, 1 H), 6.54-6.58 (m, 1 H), 7.04-7.11 (m, 2 H), 7.41-7.60 (m, 9 H), 7.89-7.94 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 38.0 (t), 43.9 (d), 48.5 (d), 49.2 (d), 49.4 (d), 51.6 (d), 60.0 (d), 126.8 (d), 127.9 (d), 128.7 (d), 129.0 (d), 129.3 (d), 129.4 (d), 129.5 (d), 129.6 (d), 129.7 (d), 131.4 (s), 134.2 (d), 136.7 (s), 137.1 (s), 142.7 (s), 144.6 (s), 146.5 (s), 155.7 (s), 156.2 (s), 198.3(s). Anal. Calcd for $C_{30}H_{22}N_2O$: C, 84.48; H, 5.20. Found: C, 84.44; H, 5.31. The structure of **6** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Base Promoted Rearrangement of 3. To a solution of **3** (200 mg, 0.84 mmol) in EtOH (20 mL) under argon was added a solution of KOH (95 mg, 1.68 mmol) in EtOH (5 mL), and the resulting mixture was refluxed for 0.5 h. Thin layer chromatographic (tlc) analysis of the reaction mixture revealed the absence of starting materials and the presence of a single reaction product. The reaction mixture was concentrated *in vacuo*., and Et_2O (20 mL) was added to the residue. The resulting ethereal solution was washed successively with H_2O (10mL), saturated aqueous NaCl (15 mL), and H_2O(10mL). The organic layer was dried ($MgSO_4$)

and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained, a yellow solid, was recrystallized from EtOAc. Pure **7** (210 mg, 88%) was thereby obtained as a colorless microcrystalline solid: mp 143-144 °C; IR ($CHCl_3$) 2980 (s), 2881 (m), 1737 (s), 1697 (s), 1352 (w), 1269 (m), 1120 (s), 794 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.16 (t, $J = 7.6$ Hz, 3 H), 1.88 (*A*B, $J_{AB} = 11.3$ Hz, 1 H), 2.01 (A*B*, $J_{AB} = 11.3$ Hz, 1 H), 2.16 (s, 1 H), 2.49-2.61 (m, 5 H), 2.85 (s, 1 H), 3.01-3.29 (m, 3 H), 3.38 (q, $J = 9.8$ Hz, 2 H), 5.34-5.40 (m, 2 H), 5.59-5.67 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.8 (q), 37.1 (t), 40.5 (d), 40.7 (d), 42.8 (t), 44.7 (d), 47.9 (d), 50.8 (d), 54.4 (d), 57.6 (d), 65.4 (s), 65.8 (t)., 67.1 (d), 86.2 (d), 130.3 (d), 133.2 (d), 212.3 (s), 224.1 (s). Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.09; H, 6.88. The structure of **7** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

X-ray Structures of 3, 4, 6, and 7. All data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[10] Pertinent X-ray data are given in Table 2. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (**3** was solved by using MULTAN[11], while **4**, **6**, and **7** were solved by using SIR[12]), and the model was refined by using full-matrix least-squares techniques. The number of atoms that were treated with anisotropic thermal parameters depended upon the number of observed reflections. In the case of **6**, all non-hydrogen atoms other than the tertiary carbon atoms were treated with anisotropic thermal parameters. For the remaining structures, sufficient data were available to refine every non-hydrogen atom in this fashion. Hydrogen atoms were located on difference maps and then were included in the model in idealized positions [$U(H) = 1.3\ B_{eq}(C)$] wherever possible. All computations other than those specified were performed by using MolEN.[13] Scattering factors were taken from the usual sources.[14] X-ray structure drawings of **3**, **4**, **6**, and **7** are shown in Figures 1-4, respectively.[15]

Table 2. X-ray data collection and processing parameters for **3**, **4**, **6**, and **7**.

Compound	3	4	6	7
Formula	$C_{16}H_{14}O_2$	$C_{16}H_{14}O_2$	$C_{30}H_{22}N_2O$	$C_{18}H_{20}O_3$
Size (mm)	0.25 x 0.25 x 0.40	0.21 x 0.24 x 0.32	0.24 x 0.28 x 0.31	0.18 x 0.22 x 0.24
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	11.7434 (6)	14.057 (2)	10.193 (1)	7.4873 (5)
b (Å)	10.4202 (6)	7.0185 (9)	13.681 (1)	14.4535 (9)
c (Å)	9.6082 (6)	12.0867 (1)	15.524 (1)	15.515 (1)
β (°)	101.701 (5)	102.704 (9)	103.337 (7)	104.138 (6)
V (Å^3)	1151.3 (1)	1163.3 (2)	2122.6 (3)	1418.3 (2)
Z-value	4	4	4	4
D_{calc} (g-cm^{-3})	1.374	1.360	1.340	1.332
μ (cm^{-1})	0.84	0.83	0.76	0.84
$2\theta_{max}$ (°)	44	50	44	44
Total reflections	1571	2316	2904	1982
Unique reflections	1497	2235	2738	1830
R_{int}	0.016	0.019	0.014	0.019
$I \geq 3\sigma(I)$	1128	1344	1486	1183
Parameters	163	163	248	190
R, R_w	0.0416, 0.0416	0.0393, 0.0366	0.0403, 0.0405	0.0442, 0.0515
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01	< 0.01	< 0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.17; -0.21	0.15; -0.21	0.17; -0.25	0.17; -0.21

Acknowledgment. We thank the Office of Naval Research (Grant N00014-94-1-1039, A. P. M.), the United States Air Force (Contract F29601-92-K-0018, A. P. M.), the Robert A. Welch Foundation [Grants B-963 (A. P. M.) and B-1202 (S. G. B.)], and the University of North Texas Faculty Research Committee (S. G. B.) for financial support of this study.

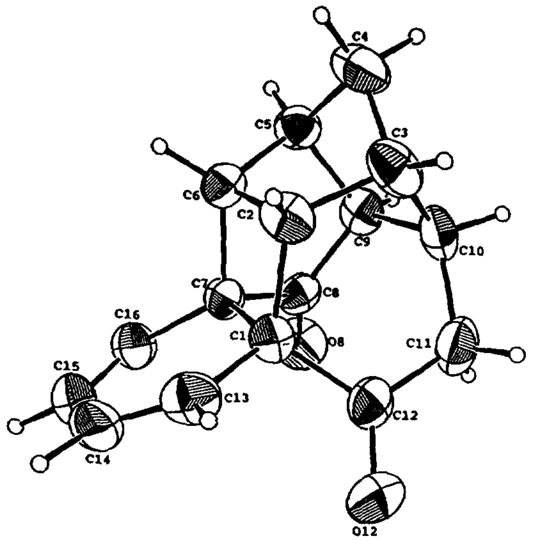


Figure 1. X-ray structure drawing of 3

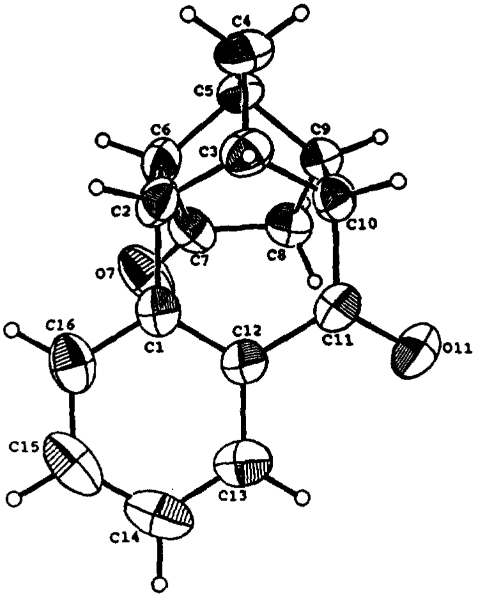


Figure 2. X-ray structure drawing of 4

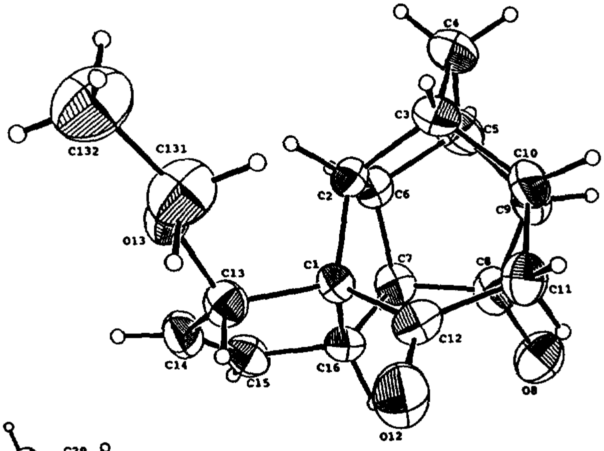


Figure 4. X-ray structure drawing of 7

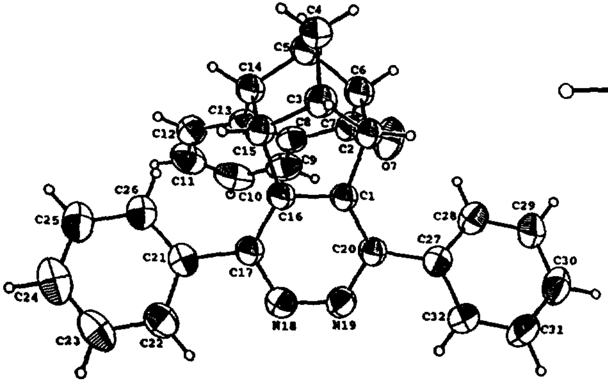


Figure 3. X-ray structure drawing of 6

References and Footnotes

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15. Tables of positional parameters, general displacement parameter expressions (U values), bond lengths, bond angles, least-squares planes, torsion angles, and intermolecular contacts for **3**, **4**, **6**, and **7** (54 + ii pages) are available upon request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CV2 1EW, U. K. Requests should be accompanied by the full literature citation for this article.

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