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Synthesis, Characterization and Crystal Density Modeling of Polycarbocyclic Oxiranes

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Abstract. Polycyclic bis-epoxides **5**, **6**, and **7** have been synthesized, and their structures established unequivocally via application of single crystal X-ray crystallographic methods. The crystal densities of **2-7** (calculated from X-ray crystallographic data) are compared with the results of theoretical density predictions. Copyright © 1996 Elsevier Science Ltd

Introduction. The importance of high density as a feature of potential fuel systems that seek to maximize net volumetric heat of combustion is well documented. The prediction of the crystal density of an unknown compound typically has been approached through the use of "volume additivity" procedures.[1] Here, the crystal molecular volume (V_{cm}) is calculated by summing appropriate crystal atomic or group volumes (V_{ca}; $V_{cm} = \Sigma V_{ca}$), and the corresponding crystal density is obtained by dividing the molecular mass (M) by V_{cm}; thus, $\rho = M/V_{cm}$. V_{ca} values usually are obtained by least-squares procedures which fit V_{cm} values to experimental crystal molecular volumes (V_{ce}) from X-ray crystal structure data (V_{ce} = unit cell volume divided by the number of molecules per unit cell) or by nonlinear least-squares methods in which the V_{ca} values are determined by fitting the experimental and calculated crystal densities. It should be noted that V_{ce} and V_{cm} are larger than the true molecular volume (V_m), because they include contributions from a certain amount of unoccupied space in the crystal lattice. The eminent Russian crystallographer Kitaigorodsky defined the packing coefficient (efficiency) as the ratio V_m/V_{ce}. The most dense materials will have large molecular densities (M/V_m) and packing coefficients.

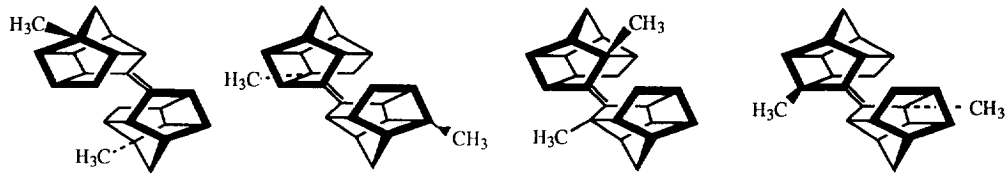
Volume additivity methods generally do not take into account crystal packing efficiency or molecular conformation effects and thus will afford identical calculated densities for positional and conformational isomers and for compounds that possess different multiples of the same functional group composition. As an

example, a volume additivity calculation predicts that 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and the various polymorphs of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) all will possess the same crystal density, 1.783 g-cm^{-3}.[1e] In fact, the experimentally observed densities of RDX, α-HMX and β-HMX differ markedly at 1.806[2] 1.839,[3] and 1.902,[4] respectively).

In 1993, Holden, Du, and Ammon[5] reported a procedure for predicting possible crystal structures of C,- H-, N-, O-, and F-containing organic compounds. Their approach involves construction of crude crystal packing arrangements (MOLPAK = MOLecular PAcKing program), starting with an optimized model (search probe) for the compound of interest, by positioning molecules around a central molecule into predetermined coordination sphere geometries. The best of these arrangements are refined subsequently with a crystal lattice energy minimization (WMIN)[6] program. This procedure takes account of molecular shape and conformation (structure of the search probe) and crystal packing efficiency.

Recently, the MOLPAK/WMIN approach was applied successfully to perform crystal density modeling calculations for four isomeric "methylated PCU alkene dimers" (**1a-1d**, Scheme 1).[7] For these examples, the observed and calculated crystal densities generally were found to agree within 1-2%.[7] We now report the results of crystal density modeling calculations that have been applied to several epoxide-functionalized polycarbocyclic systems, i. e., cage-functionalized oxiranes (**2-4**) and epoxy-derivatives of tetrahydro- and hexahydromethanonaphthalenes (**5-8**, Scheme 2).

Scheme 1



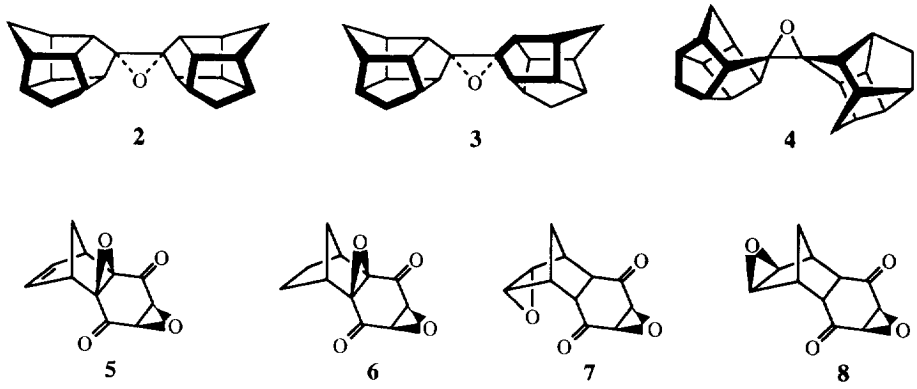
1a: D_{obs} = 1.286 g-cm^{-3} (D_{calc} = 1.255 g-cm^{-3})[7]

1b: D_{obs} = 1.212 g-cm^{-3} (D_{calc} = 1.220 g-cm^{-3})[7]

1c: D_{obs} = 1.251 g-cm^{-3} (D_{calc} = 1.254 g-cm^{-3})[7]

1d: D_{obs} = 1.262 g-cm^{-3} (D_{calc} = 1.255 g-cm^{-3})[7]

Scheme 2

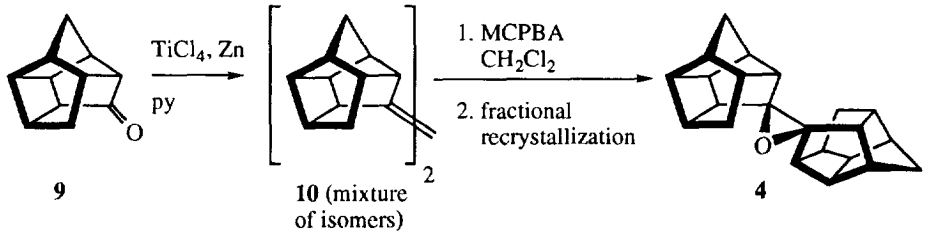


2 **3** **4**

5 **6** **7** **8**

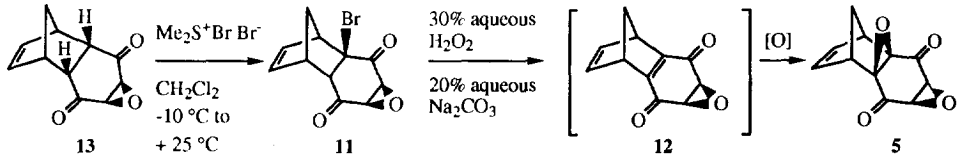
Syntheses of Functionalized Oxiranes. The syntheses of **2** and **3** have been reported previously.[8] Compound **4** was prepared via the method shown in Scheme 3.

Scheme 3



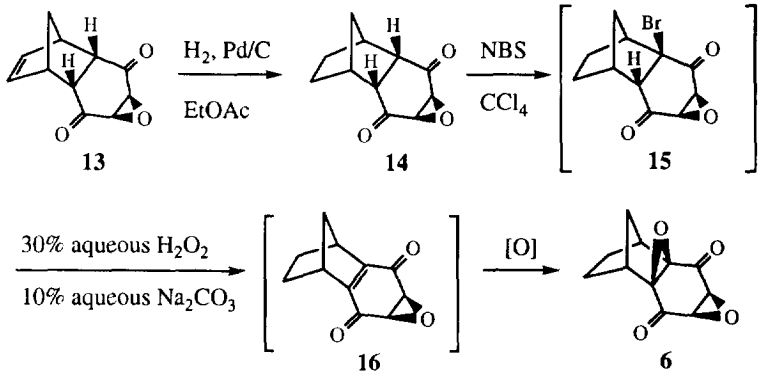
Compound **5** was synthesized by using the method shown in Scheme 4. Thus, reaction of **11** with H_2O_2 in the presence of base results in elimination followed by epoxidation of the carbon-carbon double bond in the resulting enedione, **12**,[9] thereby affording the corresponding bis-epoxide, **5**.

Scheme 4



Our synthesis of **6** is shown in Scheme 5. Catalytic hydrogenation of **13**[9a] afforded **14**, which was reacted subsequently with *N*-bromosuccinimide. The resulting α–bromoketone, **15**, was not isolated; instead, it was reacted *in situ* with basic aqueous H_2O_2. This reaction most likely proceeded via base promoted elimination of HBr in **15** to produce the corresponding enedione, **16**, which was oxidized *in situ*, thereby affording **6** (24% overall yield from **14**).

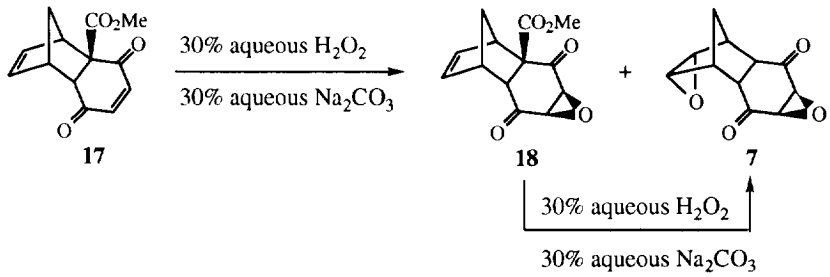
Scheme 5



Finally, **7** was synthesized from **17**[10] by using the method shown in Scheme 6. Thus, reaction of **17** with basic aqueous H_2O_2 resulted in formation of two products, **18** and **7**. In a separate experiment, **18** was converted to **7** under these same reaction conditions, thereby suggesting that **18** may indeed be an intermediate in the formation of **7** from **17**.

Compound **8** could be synthesized by following a previously published procedure.[11] However, this compound proved to be only sparingly soluble in common organic solvents, and we were unable to obtain a good quality single crystal of **8**.

Scheme 6



Crystal Density Calculations. The calculation (prediction) of the crystal density for an unknown compound follows from the prediction of the most likely crystal structure. The starting point is for this procedure requires an accurate three-dimensional model (search probe) for the material of interest. The MOLPAK[5] program creates hypothetical packing arrangements (crystal structures) about a central molecule (search probe) that mimic the molecular coordination geometries of known crystal structures. The best of the arrangements thereby obtained are refined via lattice energy minimization (WMIN program[6]), which optimizes the unit cell parameters and also the search probe orientation and position. The structure/conformation of the search probe is fixed in both the MOLPAK and WMIN steps.

A complete MOLPAK search involves 23 coordination geometries that create crystal structures in the P1, P-1, $P2_1$, $P2_1/c$, Cc, C2, C2/c, $P2_12_12_1$, $Pca2_1$, $Pna2_1$ and Pbca space groups. Most of the space groups are described by two or more geometries. For each of the coordination geometries, all unique orientations (rotation about 3 Eulerian axes from -90°to +90°in 10° steps for 19^3 = 6,859 orientations) of the search probe are used to generate hypothetical packing arrangements. The 25-50 arrangements for each geometry with the smallest unit cell volume/molecule (highest density) subsequently are refined by WMIN. The entire sequence is implemented and controlled by a UNIX shell script called "runjobs".

The search probe models were built by using either Chem3D[12] (Macintosh) or MacroModel[13] (IBM RS6000 platform) and subsequently were optimized with the AM1 semiempirical (MOPAC[14] or SPARTAN,[15] IBM RS6000 platform) and *ab initio* 3-21G* basis set (Gaussian-94,[16] IBM RS6000 and DEC 3000/400S platform) molecular orbital procedures. Compound **3** also was optimized at the 6-31G* level (Gaussian-94,[16] IBM RS6000 platform). Atom-centered point charges for the WMIN calculations were obtained for all models by using a 6-31G* basis set and ESP/CHELPG procedure (Gaussian-94,[16] IBM RS6000 platform). The "runjobs" calculations (*vide supra*) were carried out on DEC 3000/400S computers and an IBM SP2 parallel processing system (Maui High Performance Computer Center).

The observed (X-ray) and calculated densities for **2**-**7** and the calculated density for **8** are summarized in Table 1. Perhaps the most informative data in the table are the Δρ values, which show the deviations of the

Table 1. Calculated and observed densities and differences for **2** - **8**

		ρ_{calcd} / Δρ (%)[a]		
Compound	ρ_{obsd}[b]	**AM1**[c] (Δρ)[a]	**3-21G***[c] (Δρ)[a]	**X-ray** (Δρ)[a]
2[8]	1.303	1.288 (-1.1)	1.293 (-0.8)	1.307 (+0.3)
3[8]	1.350	1.292 (-4.3)	1.301 (-3.6)[d]	1.345 (-0.4)
4	1.300	1.299 (-0.1)	1.294 (-0.5)	1.312 (+0.9)
5	1.537	1.505 (-2.1)	1.535 (-0.1)	1.555 (+1.2)
6	1.511	1.479 (-2.1)	1.488 (-1.5)	1.514 (+0.2)
7	1.511	1.484 (-1.8)	1.499 (-0.8)	1.507 (-0.3)
8	- -	1.488		

[a] ρ_{obsd} = predicted density (g-cm^{-3}); Δρ (%) = 100(ρ_{calcd} - ρ_{obsd}) /ρ_{obsd}.
[b] Observed density (g-cm^{-3}) from X-ray structure determination.
[c] "AM1", "3-21G*", and "X-ray" indicate the method by which the search probe models were obtained. Carbon-hydrogen bond distances in all models were adjusted to 1.098 Å.
[d] Geometry optimization was performed by using a 6-31G* basis set.

predicted densities from the corresponding observed values as percentages of the observed values. Negative and positive Δρ values indicates that the calculated densities are smaller and larger, respectively, than observed. Clearly, the quality of correlation is poorest for those predictions which utilize an AM1 geometry-optimized search probe (average |Δρ| = 1.9%). The quality improves when *ab initio*-derived search probes are used (average |Δρ| = 1.2%). The best results were obtained by using X-ray-derived search probes (average |Δρ| = 0.5%).

The molecular volumes calculated by using the three search probe models are shown in Table 2. The trend in the molecular volumes observed when proceding from the AM1 search probe (largest) to the X-ray search probe (smallest) is the inverse of the trend in the predicted densities. This volume/density relationship is logical, since, all things being equal, crystal density is inversely proportional to molecular volume. For **3**, the 0.044 g-cm^{-3} increase in predicted density found when proceeding from the 6-31G*-derived to the corresponding X-ray-derived search probe calculations cannot be rationalized simply from observed differences in the search probe volumes (276.2 *vs.* 276.0 Å^3). Subtle structural changes most probably are at work here which may result in small differences in packing efficiencies. The results of these calculations suggest that the structural accuracy of the search probe could be a critical factor in determining the reliability of the calculated densities.

Table 2. Calculated molecular volumes for **2** - **7**[a]

Compound	AM1	3-21G*	X-ray[b]
2	278.2	278.7	275.4
3	278.2	276.2[c]	276.0
4	279.5	279.7	275.9
5	159.7	158.7	156.3
6	165.0	164.4	164.2
7	164.1	164.5	163.7

[a]Molecular volumes (Å^3) were calculated with the MacroModel[13] volume function (0.1 Å integration grid). [b]AM1, 3-21G* and X-ray indicate the manner in which search probes models were obtained. The carbon-hydrogen bond distances in all models were adjusted to 1.098 Å.
[c]Geometry optimization obtained by using a 6-31G* basis set.

Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0362.

Synthesis of 4. *m*-Chloroperbenzoic acid (MCPBA) promoted epoxidation of a CH_2Cl_2 solution of a mixture of isomeric $C_{11}H_{22}$ alkenes, **10** [synthesized via titanium promoted reductive dimerization[17] of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (**9**)],[18] was performed at ambient temperature by using a previously described procedure.[8] Workup of the reaction mixture afforded a mixture of isomeric epoxides as a colorless microcrystalline solid: mp 143-147 °C in essentially quantitative yield. Repeated fractional recrystallization from hexane of the mixture of isomeric epoxides thereby obtained afforded a single, isomerically pure epoxide, i. e., **4**, as a colorless microcrystalline solid: mp 127.5-128 °C; IR (KBr) 2950 (s), 2861 (s), 1430 (w), 1300 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.18 (ddt, J = 16.5, 12.0, 3.8 Hz, 2 H), 1.34 (br d, J = 11.0 Hz, 2 H), 1.46 (d, J = 16.0 Hz, 1 H), 1.60 (d, J = 15.5 Hz, 1 H), 1.76 (d, J = 10.5 Hz, 1 H), 1.79 (d, J = 10.5 Hz, 1 H), 1.97 (m, 2 H), 2.03 (d, J = 12.0 Hz, 2 H), 2.19 (m, 2 H), 2.37 (m, 2 H), 2.50 (m, 1 H), 2.62 (m, 4 H), 2.78 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 29.2 (t), 29.5 (t), 35.2 (t), 36.1 (t), 36.3 (d), 37.1 (d), 37.2 (d), 39.9 (d), 40.2 (d), 41.5 (d), 42.6 (d), 42.8 (d), 43.0 (d), 43.4 (d), 44.6 (d), 45.2 (d), 45.3 (d), 45.8 (d), 46.82 (d), 47.8 (d), 72.5 (s), 73.3 (s). Anal. Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.98; H, 8.32. The structure of **4** was established unequivocally via application of X-ray crystallographic techniques (*vide infra*).

Reaction of 11 with Basic Hydrogen Peroxide. A solution of **11** (100 mg, 0.37 mmol) in acetone (2 mL) was cooled externally via application of an external ice-water bath. To this cooled solution was added with stirring 20% aqueous Na_2CO_3 (1 mL, excess) and 30% aqueous H_2O_2 (1 mL, excess). The external ice-water bath then was removed, and the resulting mixture was stirred at ambient temperature overnight. Water (15 mL) was added, and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 15 mL). The organic layer was washed sequentially with water (2 x 10 mL) and brine (10 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel (250-400 mesh) by eluting with 20% EtOAc-hexane. Pure **5** was thereby obtained as a colorless microcrystalline solid: mp 122.0-122.5 °C; IR (nujol) 2985 (s), 1718 (s), 1615 (m), 1130 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.48 (*AB*, J_{AB} = 8.2 Hz, 1 H), 1.58 (*AB*, J_{AB} = 8.6 Hz, 1 H), 3.31 (s, 2 H), 3.64 (s, 2 H), 6.46 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 40.9 (t), 42.6 (d), 58.9 (d), 75.9 (s), 141.6 (d), 195.3 (s). Anal. Calcd for $C_{11}H_8O_4$: M_r^+ 204.04225. Found (high-resolution mass spectrometry): M_r^+ 204.04221. The structure of **5** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

1aα,2aβ,3β,4,5,6β,6aβ,7aα-Octahydro-3,6-methanonaphth[2,3-*b*]oxirene-2,7-dione (14). A solution of **13**[9a] (300 mg, 1.56 mmol) in EtOAc (30 mL) was hydrogenated over 10% Pd/C (30 mg, catalytic amount) by using 32 psig H_2 in a Parr shaker apparatus during 8 h, by which time H_2 uptake had ceased. The reaction mixture was filtered to remove spent catalyst, and the filtrate was concentrated *in vacuo*. The residue, a colorless solid, was recrystallized from CH_2Cl_2-hexane. Pure **14** (290 mg, 96%) was thereby obtained as a colorless microcrystalline solid: mp 202-203 °C; IR (nujol) 2980 (s), 1718 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.20-1.48 (m, 6 H), 2.69 (br s, 2 H), 3.14 (br s, 2 H), 3.62 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 22.8 (t), 37.6 (t), 38.2 (d), 48.5 (d), 59.2 (d), 204.6 (s). Anal Calcd for $C_{11}H_{12}O_3$: C, 69.46; H, 5.30. Found: C, 69.70; H, 5.69.

1aα,2aβ,3β,6β,6aβ,7aα-Hexahydro-3,6-methanonaphth[2,3-*b*]oxirene-2,7-dione (6). To a solution of **14** (255 mg, 1.33 mmol) in CCl_4 (10 mL) was added *N*-bromosuccinimide (NBS, 246 mg, 1.33 mmol). The resulting mixture was refluxed with stirring and was simultaneously irradiated with a 250 W flood lamp during 20 minutes. The reaction mixture then was cooled and filtered, and the filtrate was washed with water (2 x 10 mL). The filtrate was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Acetone (30 mL) was added to the residue, and 10% aqueous Na_2CO_3 (10 mL, excess) and 30% aqueous H_2O_2 (5 mL, excess) was added. The resulting mixture was stirred at 25 °C for 12 h and then was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (50 mL), and the resulting solution was washed with water (2 x 10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 1:1 CH_2Cl_2-hexane. Pure **6** (65 mg, 24%) was thereby obtained as a colorless microcrystalline solid: mp 122.0-122.5 °C; IR (nujol) 2955 (s), 1715 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.22-1.74 (m, 6 H), 2.90 (br s, 2 H), 3.68 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.4 (t), 27.2 (t), 36.5 (d), 59.6 (d), 76.2 (s), 227.8 (s). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.28; H, 5.00.

Bromination of 13. A solution of **13**[9a] (2.00 g, 10.6 mmol) in CH_2Cl_2 (20 mL) under argon was cooled to -10 °C via application of an external ice-salt bath. To this cold solution was added $Me_2SBr^+Br^-$ (2.4 g, 10.7 mmol). The external cold bath was removed, and the reaction mixture was allowed to warm gradually with stirring to ambient temperature during 4 h. The reaction was quenched via dropwise addition of 10% aqueous $NaHCO_3$ (20 mL) during 0.5 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The organic extracts were washed with brine (15 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 10% EtOAc-hexane. The first chromatography fractions afforded a small amount of pure **11** (510 mg, 18%) as an oil; IR (nujol) 2980 (s), 1724 (s), 1710 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.85 (d, J = 9.8 Hz, 1 H), 2.1 (d, J = 9.8 Hz, 1 H), 3.39-3.80 (m, 5 H), 5.95 (m, 1 H), 6.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 44.9 (d), 45.8 (q), 53.7 (d), 57.2 (d), 59.7 (d), 60.1 (s), 61.9 (d), 135.2 (d), 140.3 (d), 196.5 (s), 201.8 (s). Compound **11** proved to be highly unstable and difficult to work with; accordingly, it was used as obtained in the next synthetic step, without further purification.

Continued elution of the chromatography column afforded additional material. Analysis and integration of the ^1H NMR spectrum of this material revealed that it consisted of a mixture of **11** (*ca.* 40%) and **13** (*ca.* 60%).

Reaction of 17 with Basic Hydrogen Peroxide. A solution of **17**[10] (400 mg, 1.7 mmol) in acetone (10 mL) was cooled externally via application of an external ice-water bath. To this cooled solution was added with stirring 30% aqueous Na_2CO_3 (5 mL, 9 mmol) and 30% aqueous H_2O_2 (5 mL, excess). After the addition of the oxidizing agent had been completed, the external cold bath was removed, and the reaction mixture was allowed to stir at ambient temperature for 5 h. The reaction mixture was filtered, and the filtrate was concentrated *in vacuo*. Water (20 mL) was added to the residue, and the resulting aqueous suspension was extracted with CH_2Cl_2 (20 mL). The organic layer was washed with brine (10 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residual oil was purified via column chromatography on silica gel by eluting with 10% EtOAc-hexane. The first chromatography fraction afforded pure **18** (105 mg, 25%) as a colorless microcrystalline solid: mp 101-102 °C; IR (KBr) 2992 (m), 2962 (m), 1728 (s),1722 (s),1457 (m), 1439 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.37 (*AB*, J_{AB} = 9.1 Hz, 1 H), 1.72 (*AB*, J_{AB} = 9.2 Hz, 1 H), 3.33 (s, 2 H), 3.53 (*AB*, J_{AB} = 3.3 Hz, 1 H), 3.59 (*AB*, J_{AB} = 3.4 Hz, 1 H), 3.82 (s, 3 H), 3.89 (d, J = 3.2 Hz, 1 H), 6.10 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 43.32 (d), 43.46 (t), 49.77 (d), 53.61 (d), 55.20 (d), 57.45 (d), 58.33 (d), 63.66 (s), 137.9 (d), 138.0 (d), 170.1 (s), 198.9 (s), 202.3 (s). Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.90; H, 4.94.

Continued elution of the chromatography column afforded pure **7** (90 mg, 25%) as a colorless microcrystalline solid: mp 165-165.5 °C; IR (KBr) 2990 (m), 1720 (s), 1457 (m), 1440 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.72 (*AB*, J_{AB} = 8.2 Hz, 1 H), 2.08 (*AB*, J_{AB} = 8.2 Hz, 1 H), 2.95 (m, 5 H), 3.69 (s, 3 H), 3.72 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 41.08 (d), 46.53 (d), 48. 08 (d), 58.03 (d), 63.60 (d), 203.47 (s); Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.86; H, 5.03.

Reaction of 18 with Basic Hydrogen Peroxide. A solution of **18** (124 mg, 0.5 mmol, prepared via reaction of **17** with basic hydrogen peroxide, *vide supra*) in acetone (3 mL) was cooled externally via application of an external ice-water bath. To this cooled solution was added with stirring 30% aqueous Na_2CO_3 (3 mL, excess) and 30% aqueous H_2O_2 (56 mg, 0.5 mmol). The external cold bath was removed, and the reaction mixture was stirred at ambient temperature for 40 h. Thin layer chromatographic (tlc) analysis of the reaction mixture indicated the absence of starting material (**18**). The reaction mixture was filtered rapidly through a fluted filter paper, and the residue was washed with acteone (10 mL). The combined filtrates were concentrated *in vacuo*, and the residue was partitioned between $CHCl_3$ (30 mL) and water (30 mL). The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 x 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel (250-400 mesh) by eluting with 20% EtOAc-hexane. Pure **7** (57 mg, 55%) was thereby obtained as a colorless microcrystalline solid: mp 165-166.5 °C. The IR, ^1H NMR, and ^{13}C NMR spectra of **7** thereby obtained were identical in all respects with the corresponding spectra obtained previously for this compound (*vide supra*).

X-ray Structure of 4. All data for **4** were collected on a Rigaku AFC6S diffractometer by using the ω–2θ scan technique with multiple scans for weak reflections, Mo Kα radiation (λ = 0.71069 Å) and a graphite monochromator. The structure was solved via direct methods,[19] and the model was refined by using a full-matrix least-squares technique.[20] Pertinent X-ray data for **4** are given in Table 3.

X-ray Structures of 5, 6, 7, 13, and 17. All data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[21] Pertinent X-ray data are given in Table 3. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (SIR[22]), 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. For **5**, no atoms were refined in this manner. 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 used as found for **6**, **7**, and **13**. However, for **5** and **17**, the hydrogen atoms so located then were included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[23] Scattering factors were taken from the usual sources.[24]

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Table 3. X-ray structure data for **4**, **5**, **6**, **7**, **13**, and **17**.

Compound	**4**	**5**	**6**	**7**	**13**	**17**
Formula	$C_{22}H_{24}O$	$C_{11}H_8O_4$	$C_{11}H_{10}O_4$	$C_{11}H_{10}O_4$	$C_{11}H_{10}O$	$C_{13}H_{12}O_5$
Size (mm)	0.48 x 0.35 x 0.25	0.21 x 0.22 x 0.41	0.21 x 0.24 x 0.32	0.15 x 0.41 x 0.52	0.22 X 0.31 x 0.41	0.41 x 0.44 x 0.51
Space Group	$P2_1/n$	Pbca	$P2_1/c$	$P2_12_12_1$	P1-bar	$P2_1/c$
a (Å)	11.596 (3)	7.9550 (9)	12.688 (3)	8.2691 (7)	6.2702 (6)	7.8294 (7)
b (Å)	12.091 (4)	9.410 (4)	8.117 (1)	9.2392 (7)	6.341 (1)	17.335 (2)
c (Å)	12.197 (4)	23.578 (3)	9.486 (2)	11.8667 (9)	12.983 (2)	9.1005 (8)
α (°)	90	90	90	90	91.09 (1)	90
β (°)	114.57 (2)	90	111.87 (3)	90	102.679 (9)	109.439 (7)
γ (°)	90	90	90	90	118.09 (1)	90
V (Å^3)	1555.3 (9)	1765.0 (3)	906.6 (5)	906.6 (1)	439.8 (1)	1164.7 (2)
Z-value	4	8	4	4	2	4
D_{calc} (g-cm^{-3})	1.300	1.537	1.511	1.511	1.436	1.416
μ (cm^{-1})	0.72	1.11	1.08	1.08	0.98	1.03
$2\theta_{max}$ (°)	50.1	44	44	50	50	44
Total reflections	3048	2486	1256	1810	1555	1613
Unique reflections	2898	1292	1201	1605	1555	1497
R_{int}	0.028	0.030	0.042	0.015	- -	0.02
$I \geq 3\sigma(I)$	1396	416	824	1291	1094	966
Parameters	305	61	136	136	127	163
R, R_w	0.050, 0.046	0.0660, 0.0625	0.0496, 0.0484	0.0443, 0.0455	0.0429, 0.0446	0.0430, 0.0436
$(\Delta/\sigma)_{max}$	0.005	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.25; -0.17	0.27; -0.21	0.18; -0.20	0.28; -0.31	0.19; -0.14	0.27; -0.24

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