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Synthesis, Characterization and Crystal Density Modeling of Spiropolycyclic Oxiranes.

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Abstract. Spiropolycyclic mono- and bis-epoxides **1-6** have been synthesized. The structures of **1-6** have been established unequivocally via application of single crystal X-ray crystallographic methods. The crystal densities of **1-6** (from X-ray crystallographic data) are compared with the results of density predictions.

Introduction. The continuing need to develop new high energy density materials for volume-limited military applications (e.g., air-breathing missile propulsion) is well documented. A primary objective when designing potential candidate hydrocarbon fuel systems is to maximize their respective solid state (crystal) densities. The procedures usually employed to estimate crystal densities rely on a "volume additivity" approach,[1] as has been noted previously.[2,3] Volume additivity involves the calculation of an "effective" molecular volume (by summing appropriate atom and group volumes), which is combined with the molecular mass to yield a density. Such an approach fails to take into account such critical features packing efficiency and/or molecular conformation effects.

Ammon and co-workers[4] developed a procedure that enables one to predict possible crystal structures (and, hence, crystal densities) of organic compounds composed of carbon, hydrogen, nitrogen, oxygen, and/or fluorine. Their procedure takes into consideration factors related to molecular shape, conformation and crystal packing efficiency and has been used successfully to perform crystal density modeling calculations for complex polycyclic hydrocarbons[2] and for polycyclic oxiranes.[3] For each compound, the calculated density was compared with the corresponding value from an X-ray crystal structure determination.

As part of a continuing program concerned with the synthesis and characterization of high energy density materials,[2,3,5] we now report the synthesis of a series of spiropolycyclic mono- and bis-epoxides, i.e., **1-6** (Scheme 1). The structures of **1-6** have been established unequivocally from single crystal X-ray diffraction analyses and the crystal densities are compared with the results of theoretical density predictions.

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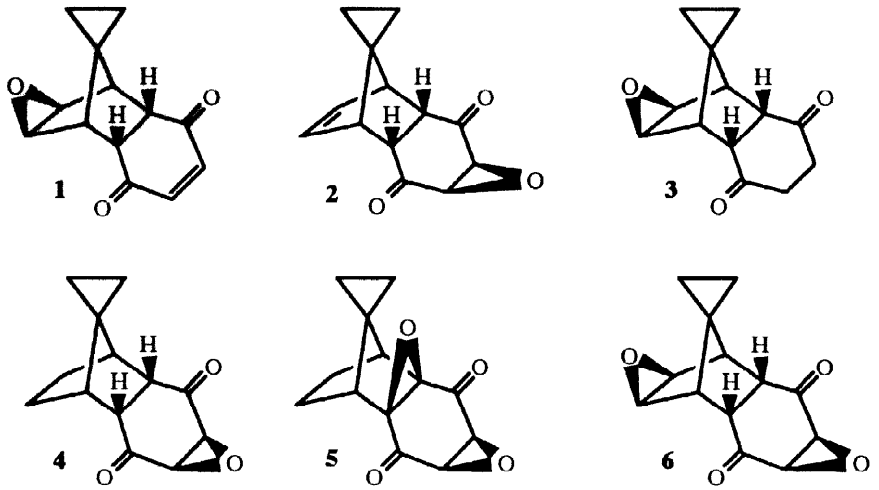
Scheme 1

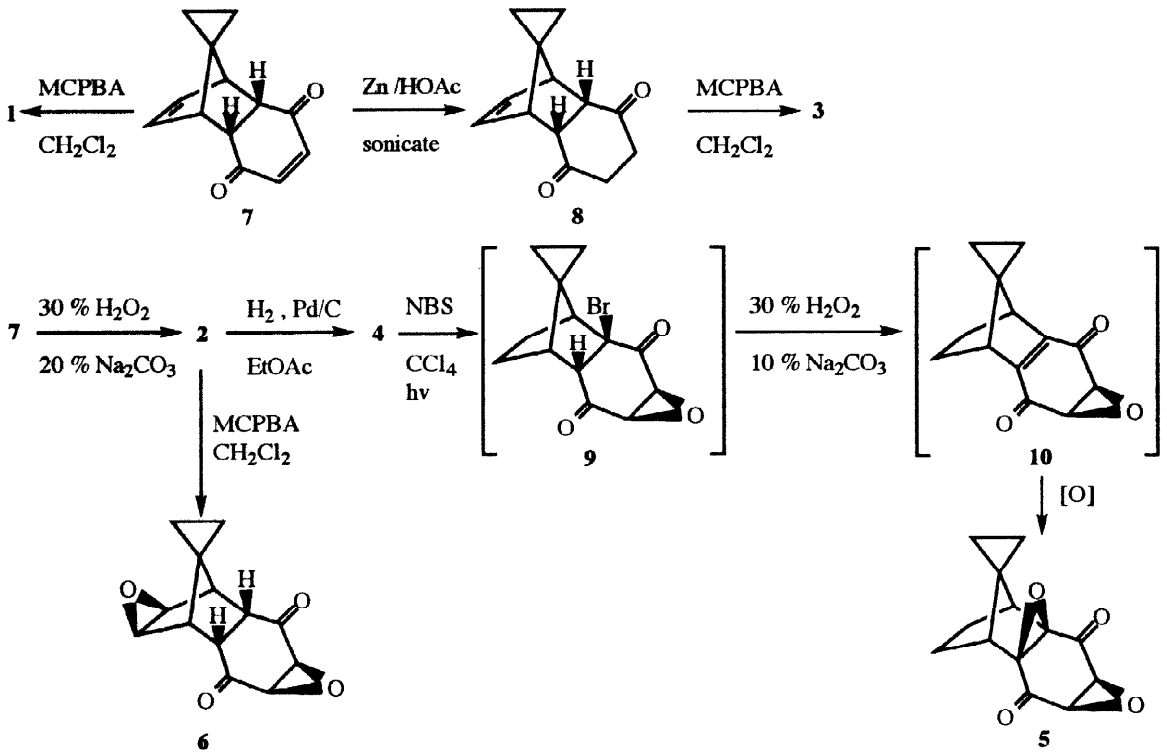


Results and Discussion. The procedure employed to synthesize **1-6** is shown in Scheme 2. Thus, **1** was prepared via MCPBA promoted epoxidation of the norbornene C=C double bond in the Diels-Alder cycloadduct of spiro[2.4]hepta-4,6-diene and *p*-benzoquinone (i.e., **7**).[6] Selective reduction of the enedione C=C double bond in **7**, performed by using Zn-HOAc,[7] afforded **8**, which subsequently could be converted into the corresponding epoxide, **3**, via facile MCPBA promoted oxidation. Selective epoxidation of the enedione C=C double bond in **7** with basic hydrogen peroxide[8] afforded **2**, which, upon reaction with MCPBA, could be converted into the corresponding bis(epoxide), i.e., **6**. Reduction of the norbornene C=C double bond in **2** was performed via catalytic hydrogenation, thereby affording **4**.

Compound **5** was prepared via a two-step, one-pot reaction sequence. Thus, **4** was brominated via its photochemical reaction with NBS-CCl_4. This was followed immediately by reaction of the putative intermediate, **9**, with basic hydrogen peroxide.[8] The latter reaction medium appears to have been sufficiently basic to promote spontaneous, *in situ* β-elimination of HBr in **9**, thereby producing **10**. Finally, air-oxidation of **10** occurred during workup to afford **5**.

Results of Crystal Density Modeling Calculations. The results of crystal structure/density modeling calculations[2-4] performed for compounds **1-6** appear in Table 1. Basically, the procedure involves the construction of hypothetical crystal structures (with appropriate translation and symmetry properties) that mimic the molecular coordination geometries found in known crystal structures. The starting point is an accurate model (the packing search probe) for the molecule of interest. Currently, the models are generated via geometry optimization with *ab initio* molecular orbital methods (density functional theory with 6-31G* basis set; B3LYP/6-31G* option in Gaussian-94 program[9]). All unique orientations (19^3 = 6,859) of a search probe are used to generate packing arrangements for each coordination geometry (total of 23 different geometries) with the MOLPAK (MOLecular PAcKing) program. The 25 highest density arrangements from each coordination geometry are refined by lattice energy minimization with the WMIN program,[10] which optimizes the unit cell parameters and search probe orientation and position. The highest density (most closely packed) structure is selected as best; the densities and predicted space groups are given in Table 1. Predicted densities from the most recent volume additivity data base compilation[1f] also are included in the table.

Scheme 2



With the exception of **2**, the predicted and observed densities have the anticipated trend of alkane monoxides (lowest) to alkene-monoxides (middle) to dioxides (highest). The average agreement ($|\Delta|$, excluding 2) of 0.77% between D_{calcd} and D_{obsd} is quite satisfactory and superior to the corresponding average $|\Delta|$ of 3.49% obtained from volume additivity (D_{VA}). The six compounds contain three pairs of constitutional isomers (**1** and **2**, **3** and **4**, **5** and **6**). D_{obsd} differs substantially from D_{calcd} for **2** and does not show a comparable density to **1**, a similarity that is found for the corresponding densities of (**3** and **4**) and (**5** and **6**). Furthermore, it should be noted that the crystal structures of **2** ($C_{13}H_{12}O_3$) and **6** ($C_{13}H_{10}O_4$) are remarkably similar, suggesting that the observed structure for **2** may not correspond to the highest density polymorph for the compound and providing a rationale for the seemingly abnormal D_{obsd}. Each of the D_{calcd} values reported in Table 1 represents the maximum predicted density from the 23 coordination geometries examined. In the case of **2**, the WMIN-calculated lattice energy for the structure that possesses D_{calcd} = 1.359 g cm^{-3} was found to be -25.79 kcal mol^{-1}, whereas the structure with the lowest lattice energy (-25.97 kcal mol^{-1}) had D_{calcd} = 1.318 g cm^{-3}, a result that stands in better agreement with D_{obsd}.

Summary and Conclusions. The data in Table 1, as well as the results of numerous predictions for other systems,[2-4] have demonstrated the superiority of the model/MOLPAK/WMIN procedure over volume additivity for accurate density estimates. Volume additivity, truly a back-of-the-envelope procedure that requires 5-10 minutes of computational time, allows rapid density estimates to be made. These data subsequently can be improved via application of highly computer-time intensive model/-MOLPAK/WMIN calculations for systems of sufficient importance and interest. The latter calculations can require from one day to one week, depending upon computer speed.

It should be noted that density is a key determinant of energetic material performance; thus, the additional time required to perform model/-MOLPAK/WMIN calculations can be justified readily on this basis, particularly when performance predictions are needed to identify new target compounds for synthesis and subsequent testing/evaluation.

Table 1. Comparison of X-ray crystal (D_{obsd}) and calculated (D_{calcd}, D_{VA}) densities (g cm^{-3}) and percent differences (Δ) for **1-6**.

Compound	D_{obsd}	D_{calcd}[a]	Δ (%)[a,b]	D_{VA}[c]	Δ (%)[c,b]
1	1.366 $P2_1/c$	1.364 P-1	-0.15	1.409	+3.15
2	1.306 P-1	1.359 C2/c	+4.06	1.409	+7.89
3	1.316 $P2_1$	1.325 $P2_1/c$	+0.68	1.382	+5.02
4	1.320[d] $P2_1/n$	1.316 $P2_1/c$	-0.30	1.382	+4.70
5	1.438 C2/c	1.409 $P2_1/c$	-2.02	1.461	+1.60
6	1.419 P-1	1.409 $P2_12_12_1$	-0.70	1.461	+2.96

[a]Calculated density and space group: MOLPAK/WMIN procedure.[4]

[b]$\Delta = 100\ (D_{calcd} - D_{obsd}) / D_{obsd}$.

[c]Calculated density: new 78 atom/group volume additivity data base.[1f]

[d]Density estimated at room temperature; X-ray density obtained at 208 K was 1.361 g cm^{-3}.

Experimental Section

Melting points are uncorrected. Elemental microanalytical data were obtained by personnel at M-H-W laboratories, Phoenix, AZ.

Synthesis of 1. A solution of **7** (200 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C by application of an external ice water bath. To this cooled solution was added dropwise with stirring a solution of MCPBA (206 mg, 1.1 mmol) in CH_2Cl_2 (5 mL), and the resulting mixture was stirred at 0 °C for 0.5 h. The external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with continuous stirring during 12 h. During this time, the progress of the reaction was monitored by tlc. The reaction was quenched via addition of 10% aqueous $NaHCO_3$ (10 mL). The resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 10 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 by eluting with 30% EtOAc-hexane, thereby affording **1** (129 mg, 60%) as a pale yellow microcrystalline solid. Fractional recrystallization of this material from CH_2Cl_2-hexane afforded pure **1** as a pale yellow microcrystalline solid: mp 161-162 °C; IR (KBr) 2970 (s), 2925 (m), 1720 (vs), 1400 (m), 1305 (m), 1200 (s), 840 (m), 750 cm-1 (m); ^1H NMR ($CDCl_3$) δ 0.10-0.35 (m, 2 H), 0.55-0.85 (m, 2 H), 2.35 (s, 2 H), 3.25 (s, 2 H), 3.55 (s, 2 H), 3.70 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.4 (t), 10.1 (t), 28.1 (s), 48.9 (d), 49.4 (d), 50.1 (d), 142.1 (d), 198.6 (s). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59; Found: C, 72.14; H, 5.57.

Synthesis of 2. A solution of **7** (100 mg, 0.5 mmol) in acetone (10 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added with stirring 20% aqueous Na_2CO_3 (5 mL) followed by 30% aqueous H_2O_2 (3 mL). After the addition of the oxidizing agent had been completed, the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with continuous stirring during 24 h. The reaction was quenched via addition of water (20 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed sequentially with water (2 x 10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from EtOAc-hexane, thereby affording pure **2** (77 mg, 72%) as a colorless microcrystalline solid: mp 87-88 °C; IR (KBr) 2970 (s), 2924 (m), 1722 (vs), 1303 (m), 1188 (s), 1010 (s), 837 (m), 754 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.34-0.42 (m, 2 H) , 0.52-0.60 (m, 2 H), 2.60-2.70 (m, 2 H), 3.50 (s, 2 H), 3.57 (t, 2 H) , 6.10 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 7.1 (t), 8.2 (t), 42.6 (s), 49.1 (d), 50.8 (d), 58.4 (d), 137.2 (d), 204.6 (s). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59; Found: C, 72.45; H, 5.70.

Synthesis of 8.[7] A 25 mL single-necked round bottomed flask was charged with glacial HOAc (10 mL), powdered Zn (850 mg, 13 g-atom) and **7** (200 mg, 1.0 mmol). The resulting mixture was sonicated in an American Brand Model ME 4.6 ultrasonic cleaner (input power 85 W) at ambient temperature. The progress of the reaction was monitored periodically by tlc analysis, and the reaction was allowed to progress until no **8** remained (*ca.* 25 minutes). The reaction then was quenched by addition of ice-cold water (10 mL). The resulting aqueous suspension was filtered through a Celite® pad, and the residue was washed with CH_2Cl_2 (10 mL). The combined filtrates were extracted with CH_2Cl_2 (3 x 10 mL), and the combined organic extracts were washed successively with water (2 x 10 mL), saturated aqueous $NaHCO_3$ (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel by eluting with 30% EtOAc-hexane. Pure **8** (161 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 60-61 °C; IR (KBr): 2991 (m), 2890 (w), 1707 (vs), 1410 (s), 1250 (m), 1145 (m), 947 (w), 736 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.35-0.50 (m, 4 H) , 2.10-2.40 (m, 2 H), 2.50-2.65 (m, 2 H), 2.71 (s, 2 H), 3.30 (s, 2 H), 6.17 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 7.4 (t) , 8.5 (t) , 38.4 (t), 44.8 (s), 52.8 (d), 53.1 (d), 137.0 (d), 209.8 (s). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.26; H, 6.87.

Synthesis of 3. A solution of **8** (200 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring a solution of MCPBA (206 mg, 1.1 mmol) in CH_2Cl_2 (5 mL), and the resulting mixture was stirred at 0 °C for 0.5 h. The external cold bath then was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with continuous stirring during 12 h. The progress of the reaction was monitored periodically via tlc analysis. The reaction was quenched via addition of 10% aqueous $NaHCO_3$ (10 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were 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 by eluting with 30% EtOAc-hexane. Pure **3** (133 mg, 62%) was thereby obtained as a colorless microcrystalline solid: mp 127-128 °C; IR (KBr): 2980 (m), 1710 (vs), 1303 (m), 1255 (w), 1159 (w), 1028 (w), 944 (w), 860 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.13-0.17 (m, 2 H), 0.63-0.70 (m, 2 H), 2.43-2.48 (m, 4 H), 2.80-2.87 (m, 2 H), 3.23-3.28 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.9 (t) , 10.6 (t), 24.7 (t), 39.2 (s), 48.3 (d), 50.8 (d), 52.9 (d), 209.1 (s).Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; Found: C, 71.62; H, 6.43.

Synthesis of 4. A solution of **2** (500 mg, 2.31 mmol) in EtOAc (25 mL) was hydrogenated over 10% palladized charcoal (30 mg, catalytic amount) in a Parr shaker apparatus by using 30 psig H_2 during 12 h, by which time hydrogen 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 recrystallised from CH_2Cl_2-hexane. Pure **4** (460 mg, 91%) was thereby obtained as a colorless microcrystalline solid: mp 140-141 °C; IR (KBr) 2958 (w), 1705 (vs), 1475(w), 1311 (m), 839 (s), (m), 758 (m), 660 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.52 (br s, 4 H), 1.33 (m, 2 H), 1.61 (m, 2 H), 1.85 (br s, 2 H), 3.38 (s, 2 H), 3.60-3.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 5.8 (t) , 6.7 (t) , 23.6 (t), 34.1 (s), 43.9 (d), 49.5 (d), 59.8 (d), 204.9 (s). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; Found: C, 71.34; H, 6.25.

Synthesis of 5. To a solution of **4** (300 mg, 1.37 mmol) in CCl_4 (20 mL) was added *N*-bromosuccinimide (NBS, 250 mg, 1.37 mmol). The resulting mixture was refluxed with stirring while being irradiated by using a 250 W flood lamp during 0.5 h. The reaction mixture was cooled to ambient temperature and filtered, and the filtrate was washed with water (3 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, followed by 10% aqueous Na_2CO_3 (10 mL, 10 mmol, excess) and 30% aqueous H_2O_2 (5 mL, 44 mmol, excess). The resulting mixture was stirred at ambient temperature 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 30% EtOAc-hexane. Pure **5** (70 mg, 22%) was thereby obtained as a colorless microcrystalline solid: mp 169-170 °C; IR (KBr) 2958 (w), 1708 (vs), 1350 (m), 1294 (w), 1213 (w), 1112 (w), 983 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.15-0.25 (m, 2 H), 0.50-0.70 (m, 2 H), 1.32-1.38 (m, 2 H), 1.70-1.85 (m, 2 H), 2.23 (s, 2 H), 3.68 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.6 (t), 9.1 (t), 25.3 (t), 26.5 (s), 43.6 (d), 60.0 (d), 68.9 (s), 204.9 (s). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21; Found: C, 67.00; H, 5.34.

Synthesis of 6. A solution of **2** (200 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added with stirring a solution of MCPBA (206 mg, 1.1 mmol) in CH_2Cl_2 (5 mL) dropwise with stirring, and the resulting mixture was stirred at 0 °C for 0.5 h. The external cold bath then was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with continuous stirring during 24 h. The progress of the reaction was monitored periodically via tlc analysis. The reaction was quenched via addition of 10% aqueous $NaHCO_3$ (10 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were 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 by eluting with 25% EtOAc-hexane. The material thereby obtained was recrystallized from EtOAc-hexane to give pure **6** (128 mg, 60%) as a colorless microcrystalline solid: mp 205-206 °C; IR (KBr) 3072 (w), 3007 (w), 2970 (m), 1724 (vs), 1315 (w), 1267 (w), 1161 (m), 1028 (m), 846 (s), 765 (m), 603 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.10-0.30 (m, 2 H), 0.60-0.80 (m, 2 H), 2.35 (s, 2 H), 3.25 (s, 2 H), 3.55 (s, 2 H), 3.70 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.7 (t) , 10.4 (t) , 24.2 (s), 45.6 (d), 49.9 (d), 50.4 (d), 59.7 (d), 203.9 (s). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21; Found: C, 67.17; H, 5.08.

X-ray Structure Determination of 1-6. All data were collected on an Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator by using the ω -2θ scan technique. Standard procedures used in our laboratory for this purpose have been described previously.[11] 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 (SIR[12]), and the models were refined by using full-matrix least-squares techniques. In **2-6**, all non-hydrogen atoms were refined by using anisotropic thermal parameters. However, in **1**, sufficient data were available to permit refinement in this fashion of only the oxygen atoms and carbon atoms in the oxirane ring. Hydrogen atoms were located on difference maps; For all compounds except **5**, these were included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)] and allowed to ride upon the attached carbon atom. However, in the case of **5**, the hydrogen atoms were refined. All computations other than those specified were performed by using MolEN.[13] Scattering factors were taken from the usual sources.[14]

Table 2. X-ray data collection and processing parameters for **1-6.**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{13}H_{12}O_3$	$C_{13}H_{12}O_3$	$C_{13}H_{14}O_3$	$C_{13}H_{14}O_3$	$C_{13}H_{12}O_4$	$C_{13}H_{12}O_4$
Size (mm)	0.10 x 0.12 x 0.13	0.11 x 0.42 x 0.63	0.13 x 0.17 x 0.40	0.12 x 0.14 x 0.16	0.32 x 0.35 x 0.41	0.13 x 0.15 x 0.16
Space Group	$P2_1/c$	P1-bar	$P2_1$	$P2_1/n$	C2/c	P1-bar
a (Å)	11.1785 (7)	6.248(1)	6.1693 (9)	6.3302 (6)	23.406 (2)	6.2354 (6)
b (Å)	8.4299 (8)	6.2437 (7)	9.4577 (9)	11.773 (1)	8.8465 (8)	6.2380 (6)
c (Å)	11.186 (1)	16.288 (1)	9.4584 (9)	14.518 (2)	10.3932 (7)	16.241 (2)
α (°)	90	80.057 (8)	90	90	90	80.284 (9)
β (°)	93.971 (7)	80.36 (1)	93.58 (1)	100.087 (8)	94.547 (6)	79.495 (9)
γ (°)	90	62.00 (1)	90	90	90	61.548 (8)
V (Å^3)	1051.6 (2)	549.9 (2)	550.8 (1)	1065.2 (2)	2145.3 (3)	543.7 (1)
Z-value	4	2	2	4	8	2
D_{calc} (g cm^{-3})	1.366	1.306	1.316	1.361	1.438	1.419
μ (cm^{-1})	0.90	0.89	0.87	0.90	1.00	0.99
T (K)	295	295	295	208	295	295
$2\theta_{max}$ (°)	40	50	50	50	50	44
Total reflections	1134	1941	2249	2140	2058	1348
Unique reflections	1075	1941	1139	1972	2015	1348
R_{int}	0.016	- -	0.019	0.027	0.016	- -
$I \geq 3\sigma(I)$	646	1209	758	1129	1298	974
Parameters	100	145	144	145	202	154
R, R_w	0.0469, 0.0471	0.062, 0.062	0.0377, 0.0372	0.0438, 0.0459	0.0334, 0.0444	0.0350, 0.0445
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
ρ_{max}; ρ_{min} (eÅ^{-3})	0.29, -0.33	0.27, -0.25	0.19, -0.20	0.22; -0.19	0.12; -0.17	0.20; -0.15

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