Experimental Section

To a 100-mL three-necked flask are added 250 mL of tetrahydrofuran (THF) and slightly more than ⅓ mol of sodium hydride (about 9 g). This mixture is cooled to between 0 and 5 °C in an ice–salt bath and kept under nitrogen gas throughout the reaction (much aldehyde oxidation occurs otherwise).

The aliphatic aldehyde (⅛ mol) and chloroform (¼ mol = 20.4 mL) is added to the flask dropwise over a period of 1–1.5 h after which the solution is stirred for an additional 3–3.5 h at the ice–salt bath temperature. (The reaction is exothermic and is likely to erupt from the flask if the temperature is allowed to rise above 20 °C.) Then 35 g of sodium hydroxide pellets dissolved in 150 mL of methanol are added to the flask dropwide with continued stirring over a period of 1 h. During the methanol addition the reaction is exothermic but the temperature is maintained below 40 °C with the ice bath. After completion of this addition, the reaction mixture is heated with a Glas-col heater and the temperature is kept in the range of 70–75 °C for a period of 2–3 h during methanolysis. The reaction mixture is allowed to stand overnight while cooling down to room temperature. Usually a yellow or pale-yellow solution containing a thick layer of white precipitate is obtained which is transferred to a beaker along with 200–250 mL of distilled water, warmed if necessary to dissolve all the inorganic products. The solution, which should be highly basic (pH 12), is cooled and extracted several times with ether to remove the neutral and basic materials. The solution is adjusted to pH 1, with hydrochloric acid. An oily layer appears on the solution surface, consisting of the α-methoxyaliphatic acid and trace impurities. This oil is removed by three 50-mL ether extractions. The ether extract is dried with sodium sulfate, refluxed with activated charcoal, and filtered and the ether is evaporated (the last traces under vacuum). The crude oils obtained suggest yields in the range of 69–80% of the theory. Vapor phase chromatograms run of these oils show impurities to average 5–8% of the crude acid giving yields before purification of 62–76% (with one exception, α-methoxyundecanoic acid, whose yield is 45%).

The purification of these oily acids is accomplished using a microdistillation system under reduced pressure. The final analytical product distillates varied in yield from 51 to 63% (24% for α-methoxyundecanoic acid).

Analytical and Spectroscopic Data of the α-Methoxyaliphatic Acids. General. Distillations were carried out using Bantam Ware apparatus. The infrared spectra were obtained on a Beckman IR-8. ^{1}H NMR spectra were obtained using a Joelco Model JNM-C-60HL and are reported in parts per million downfield from internal tetramethylsilane. The indicated yields are amounts obtained after careful distillation, one fraction of which was analytically pure.

2-Methoxyheptanoic acid: bp 246–250 °C; yield 54%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1190, 1120, 1095, 720 cm^{-1}; NMR (CDCl$_3$) δ 0.98 (3 H, triplet), 1.45 (8 H, complex), 3.44 (3 H, singlet), 3.69 (1 H, triplet), 13 (1 H, singlet). Anal. Calcd for $C_8H_{16}O_3$: C, 59.97; H, 10.06; OCH$_3$, 19.37. Found: C, 60.00; H, 10.14; OCH$_3$, 18.93.

2-Methoxyoctanoic acid: bp 49–52 °C (12 mmHg); yield 53%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1190, 1120, 1095, 720 cm^{-1}; NMR (CDCl$_3$) δ 0.98 (3 H, triplet), 1.40 (10 H, complex), 3.42 (3 H, singlet), 3.75 (1 H, triplet), 13.1 (1 H, singlet). Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41; OCH$_3$, 17.81. Found: C, 61.97; H, 10.24; OCH$_3$, 18.12.

2-Methoxy-3,4-dimethylhexanoic acid: bp 246–250 °C; yield 56%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1360, 1195, 1095, 940 cm^{-1}; NMR (CDCl$_3$) δ 0.98 (9 H, complex), 1.8 (4 H, complex), 3.52 (3 H, singlet), 3.78 (1 H, complex), 13.45 (1 H, singlet). Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41; OCH$_3$, 17.81. Found: C, 62.01; H, 10.34; OCH$_3$, 17.53.

2-Methoxy- 3-methylbutanoic acid: bp 197–201 °C; yield 59%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1375, 1160, 1190, 1095, 980–900 cm^{-1}; NMR (CDCl$_3$) δ 1 (6 H, quartet), 2.1 (1 H, septet), 3.56 (1 H, doublet), 3.48 (3 H, singlet). Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.58; H, 9.06.

2-Methoxpentanoic acid: bp 193–197 °C; yield 57%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1190, 1120, 1095, 720 cm^{-1}; NMR (CDCl$_3$) δ 0.97 (3 H, triplet), 1.65 (4 H, complex), 3.45 (3 H, singlet), 3.72 (1 H, triplet), 13.9 (1 H, singlet). Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15; OCH$_3$, 23.48. Found: C, 54.38; H, 9.16; OCH$_3$, 23.53.

2-Methoxyhexanoic acid: bp 47–50 °C (13 mmHg); yield 53%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1190, 1120, 1095, 720 cm^{-1}; NMR (CCl$_4$) δ 0.98 (3 H, triplet), 1.42 (6 H, complex), 3.43 (3 H, singlet), 3.69 (1 H, triplet), 12.8 (1 H, singlet). Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65; OCH$_3$, 21.22. Found: C, 57.37; H, 9.74; OCH$_3$, 20.69.

2-Methoxynonanoic acid: bp 260–264 °C; yield 54%; IR$_{max}$ (neat) 3200–2500, 1700, 1420, 1195, 1110, 1095, 940, 720 cm^{-1}; NMR (CDCl$_3$) δ 0.98 (3 H, triplet), 1.43 (12 H, complex), 3.45 (3 H, singlet), 3.77 (1 H, triplet), 13.2 (1 H, singlet). Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71; OCH$_3$, 16.48. Found: C, 63.83; H, 10.59; OCH$_3$, 16.62.

2-Methoxydecanoic acid: bp 278–281 °C; yield 51%; IR$_{max}$ (neat) 3200–2500, 1705, 1420, 1095, 720 cm^{-1}; NMR (CCl$_4$) δ 0.98 (3 H, triplet), 1.42 (14 H, broad complex), 3.45 (3 H, singlet), 3.77 (1 H, triplet), 13.5 (1 H, singlet). Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.69. Found: C, 65.37; H, 10.96.

2-Methoxy-2-cyclohexylethanoic acid: bp 241–245 °C; yield 63%; IR$_{max}$ (neat) 3200–2500, 1700, 1410 (doublet), 1110, 950–880 (broad) cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.79; H, 9.36.

Registry No.—2-Methoxyheptanoic acid, 64769-03-5; 2-methoxyoctanoic acid, 66018-23-3; 2-methoxy-3,4-dimethylhexanoic acid, 66018-24-4; 2-methoxy-3-methylbutanoic acid, 66018-25-5; 2-methoxypentanoic acid, 66018-26-6; 2-methoxyhexanoic acid, 66018-27-7; 2-methoxynonanoic acid, 66018-28-8; 2-methoxydecanoic acid, 66018-29-9; 2-methoxy-2-cyclohexylethanoic acid, 15540-18-8; hexanal, 66-25-1; heptanal, 111-71-7; 2,3-dimethylpentanal, 32749-94-3; 2-methylpropanal, 78-84-2; butanal, 123-72-8; pentanal, 110-62-3; octanal, 124-13-0; nonanal, 124-19-6; cyclohexanecarboxaldehyde, 2043-61-0; chloroform, 67-66-3; sodium hydride, 7646-69-7; tetrahydrofuran, 109-99-9.

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Revision of the Stereochemical Assignment of a Cyclobutane Derivative from Chalcone Photodimerization via X-ray Diffraction Analysis

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In a previous report[2] some of us described the stereochemistry of a chalcone photodimer as having β-truxinic structure **1**. This stereochemical assignment was made essentially on the basis of ^{1}H-NMR data and their comparison with data for a number of structurally related compounds. Subsequently, because the two internal rotation angles θ_1 and θ_2 of the benzoyl groups permit different conformational preferences, we wished to compare the conformation in the solid state with that derived from our data in solution. Furthermore, we wanted to determine if the cyclobutane ring was puckered out of the plane because of the four bulky substituents attached to it. In fact, few data exist in the literature[3,4] about the solid-state structure of cyclobutane derivatives in which no bonds of the four-membered ring are inserted in a fused structure or in which each carbon of the ring bears one substituent.

For these reasons, an x-ray structure determination was

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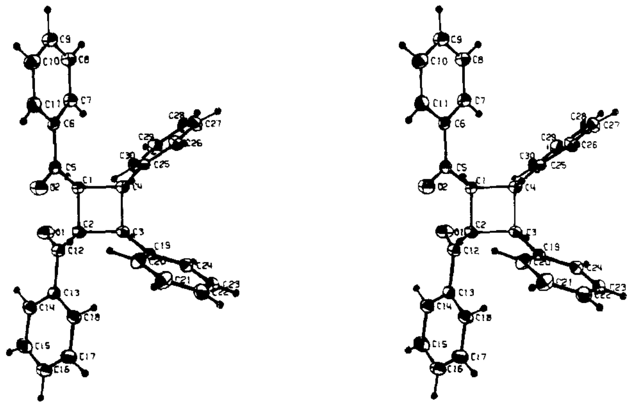


Figure 1. Stereoscopic view of a single molecule of **2**.

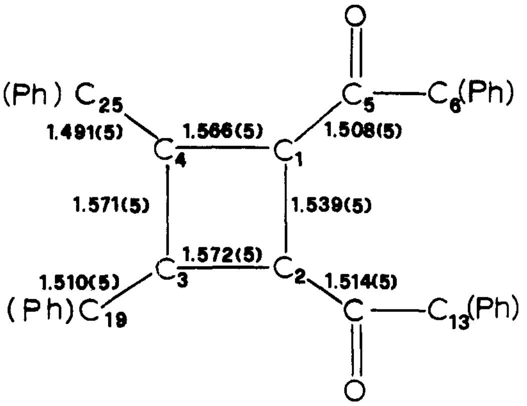
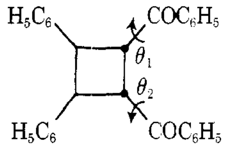
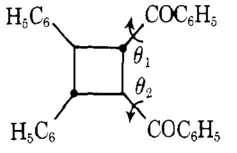


Figure 2. Selected bond distances and partial numbering scheme.

undertaken. The relative stereochemistry found in this study shows a δ-truxinic structure **2**, thus our previous assignment of structure **1** was incorrect.



1



2

The three-dimensional structure of this photodimer of chalcone (mp 126 °C) was determined by x-ray structure analysis of crystals obtained from ethyl alcohol solution. A single colorless crystal was used to collect 2056 observed reflections with $2\theta < 130°$ on a Syntex $P2_1$ diffractometer (Cu Kα radiation). The space group is monoclinic, $P2_1/c$, with four molecules per unit cell: a = 10.902 (4) Å; b = 9.671 (4) Å; c = 21.426 (6) Å; and β = 90.69 (3)°; ρ_{obsd} = 1.22 g cm^{-3}; ρ_{calcd} = 1.222 g cm^{-3}. The structure was solved by direct methods[5] and refined by full-matrix least squares (for all nonzero reflections) to an unweighted R factor of 0.059 and a weighted R factor of 0.057.[6] Anisotropic temperature factors were used for all non-hydrogen atoms.

A stereoscopic drawing of one molecule is shown in Figure 1; bond distances in the ring and a partial numbering scheme are given in Figure 2. The bond lengths and bond angles are in general close to accepted values. Remarkably, bond lengths C2–C3, C3–C4, and C1–C4 are longer than normal C–C single bonds but their values are not unusual in substituted cyclobutanes.[3,4] There are no close contacts between molecules in the crystal.

The four-membered ring is slightly nonplanar; the torsion angles are in fact C1–C2–C3–C4 7.23°, C1–C4–C3–C2 −7.10°, C2–C1–C4–C3 7.25°, and C3–C2–C1–C4 −7.25°. Hence no other structures have been reported with an intermediate degree of puckering, i.e., in the range 1–18°.[4]

Torsion angles of the two benzoyl groups are C2–C1–C5–C6 176.58° and C1–C2–C12–C13 −172.83°, while torsion angles of the two phenyl groups are C1–C4–C25–C26 139.12° and C2–C3–C19–C20 −28.82°. Angle ABCD is considered positive if, when looking along the B–C bond, A has to be rotated clockwise to eclipse B, according to a well-known convention.[7]

The intramolecular nonbonded distance O1- - -O2 is 4.31 Å.

The preferred conformation is thus well inside the energetically allowed area generated as a function of the internal rotation angles θ_1 and θ_2 of the benzoyl groups in an energy exclusion map.[8]

Acknowledgments. We thank Professor I. C. Paul, Department of Chemistry, University of Illinois, Urbana, for the use of facilities in his x-ray laboratory.

Registry No.—**2**, 24825-07-8.

Supplementary Material Available: Tables of atomic coordinates in fractions of the unit cell parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

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Carbon Acidity. 57. Equilibrium Acidities of *o*- and *p*-Benzylbiphenyl. Steric Inhibition of Acidity

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We have previously reported[1] a number of relative ion pair acidities (pK_{CsCHA}) based on competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA).

$$R_1H + R_2^-Cs^+ \rightleftarrows R_1^-Cs^+ + R_2H \qquad (1)$$

$$K = [R_2H][R_1^-Cs^+]/[R_1H][R_2^-Cs^+] \qquad (2)$$

$$\log K = pK(2) - pK(1) \qquad (3)$$

We report in this note the pK_{CsCHA} values obtained for the title hydrocarbons.[2] The results provide an assessment of the *o*-phenyl steric effect on the carbon acidity of diarylmethanes.[3]

Results and Discussion

Spectral data not reported previously are summarized in Table I. Table II gives results for the individual equilibrium runs.

Table I. Absorption Maxima for Cesium Salts in Cyclohexylamine

Hydrocarbon	λ_{max}, nm	$10^{-3}\epsilon$
o-BBP (*o*-benzylbiphenyl)	460	36.0 ± 1.4
p-BBP (*p*-benzylbiphenyl)	525	65.0 ± 2.7

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