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(5) *threo*-3-Methyl-2-pentyl acetate (**3**) has been synthesized by hydroboration of *trans*-3-methyl-2-pentene and acetylation.[1]

(6) *erythro*-3-Methyl-2-pentyl acetate (**4**) was obtained by acetylation of a nearly 1:1 diastereomeric mixture of commercially available 3-methyl-2-pentanol. Both the erythro and the threo isomer of the resulting acetates could be isolated in pure form by preparative scale GC (see Experimental Section).

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The Crystal and Molecular Structures of *S*-(+)-2,2-Diphenylcyclopropanecarboxylic Acid and of *R*-(+)-2,2-Diphenyl-1-methylcyclopropanecarboxylic Acid. A Study of the Environments of Gas–Solid Reactions That Exhibit Anisotropic Behavior

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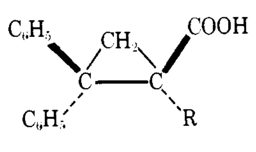
Abstract: The crystal structures of *S*-(+)-2,2-diphenylcyclopropanecarboxylic acid (I) and of *R*-(+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid (II) have been determined to examine the environment of some gas-solid reactions. The crystals of I are monoclinic, $a = 14.657(5)$, $b = 6.238(2)$, $c = 7.967(3)$ Å and $\beta = 117° 15'(2')$; there are two molecules of I in the space group $P2_1$. The structure was refined to an R factor of 0.043 on 1066 independent nonzero reflections. The crystals of II are orthorhombic, $a = 18.199(5)$, $b = 6.309(1)$, and $c = 11.796(2)$ Å; there are four molecules in the space group $P2_12_12_1$. The structure has been refined to an R factor of 0.037 on 1261 independent nonzero reflections. The molecular structures of I and II are very similar and the bond lengths in the cyclopropane ring show the influence of the exocyclic unsaturated substituents. Both structures exhibit linear chains or catemers formed by hydrogen bonding of the carboxylic acid groups along the b direction. In the crystal of I the b axis is polar and all the chains run in the same direction, whereas in II chains run in alternate directions along b. In both structures, the polar groups in the chains are well insulated from these groups in adjacent chains by nonpolar hydrocarbon groups, thus explaining the observed *ditropic* attack of ammonia gas on single crystals of I and II.

In studies[1-5] of the reactions of crystalline acids with ammonia and with gaseous amines the enantiomeric cyclopropane acids I and II are of particular interest. Whereas most acids crystallize as cyclic hydrogen-bonded dimers,[6] the enantiomeric acids I and II had been thought[7,8] to crystallize as hydrogen-bonded chains, or catemers.[6] A preliminary communication[4] reported the crystal structure and reaction of single crystals of the methyl acid II with ammonia gas, a reaction found to be ditropic, that is to proceed primarily along the two directions parallel to the hydrogen-bonded chains. The structure reported in preliminary form[4] has subsequently been discussed by Leiserowitz[6] in relation to the structures of other carboxylic acids. A second preliminary communication[5] has described the use of the acid I in a study of the selective reaction of gaseous optically active phenylethylamine with crystals of a single enantiomeric form of I.



R-(−)-**I**, R = H
R-(+)-**II**, R = CH_3

This paper presents the crystal structures of resolved forms of the acids I and II on which the preliminary communications[4,5] were based, and also provides additional information about these solid–gas reactions. The x-ray structural work was

Table I. Reaction of (+)-α-Phenylethylamine Vapor with Single Crystals of (+)- and (−)-2,2-Diphenyl-1-methylcyclopropanecarboxylic Acid ((+)- and (−)-II)

Time, h	Enantiomeric Acid	Wt, g	% N[a]	% reaction	Ratio (−)/(+)
3.5	(+)	0.3121	0.7	18	
3.5	(−)	0.2445	2.0	51	2.8
7	(+)	0.0844	2.0	51	
7	(−)	0.1897	2.3	59	1.2

[a] Theoretical percent N for formation of a 1:1 salt is 3.9%.

actually carried out on resolved crystals of *S*-(+)-I and *R*-(+)-II. However, to facilitate comparisons of the structures of I and II, the x-ray results on I are presented as if they corresponded to the *R*-(−) enantiomer. The absolute configurations are based on the assignments of Walborsky and collaborators[8] and have not been established by anomalous dispersion x-ray methods.

Experimental Section

***R*-(−)- and *S*-(+)-2,2-Diphenylcyclopropanecarboxylic Acid.** *R*- and *S*-I were prepared and resolved by the method of Walborsky and Hornyak.[9] Crystallization from methanol gave needles: optical goniometry, angle found (calcd): (crystal type 1) (100):(001) 63° (63°), $\underline{1}$00):(10$\bar{1}$) 85° (85°); (crystal type 2) (001):(100) 64° (63°), (001):($\bar{1}$01) 32° (33°).

***R*-(+)-2,2-Diphenyl-1-methylcyclopropanecarboxylic acid** was prepared and resolved by the method of Walborsky and Hornyak.[9] Slow evaporation from acetone gave colorless plates.

Reactions of the acids with ammonia and with amines were carried out as described previously.[1,5]

A rough estimate of the relative rates of reaction of the (+)-phenylethylamine with (+)- and (−) acids II was obtained by carrying out reaction of several crystals of each isomer with phenylethylamine vapor as before and submitting the product for a quantitative analysis for nitrogen as a measure of the uptake of the amine. The results are shown in Table I.

X-Ray Structure Determination of *S*-(+)-2,2-Diphenylcyclopropanecarboxylic Acid (*S*-(+)-I). Crystal Data. $C_{16}H_{14}O_2$ has a molecular weight of 238.3: monoclinic, a = 14.657(5), b = 6.238(2), c = 7.967(3) Å, β = 117° 15′(2′), V = 647.6 Å^3, Z = 2, ρ_c = 1.22 g cm^{-3}, F(000) = 252, μ(Cu Kα) = 6.5 cm^{-1}. Systematic absences, 0k0 when $k = 2n + 1$, plus the fact that the molecules of I are chiral established the space group as $P2_1$. Cell data were obtained by a least-squares fit to the settings for 11 hand-centered reflections (Cu Kα, λ 1.54178 Å). Intensity data were collected on a Picker FACS-1 diffractometer. The reflections with $2\theta \leq 130°$ were measured by the θ-2θ scan technique at a scan rate of 1 deg min^{-1}. The basewidth was 2° with a dispersion correction being applied to account for the α_1-α_2 splitting; backgrounds at each limit of the scan were measured for 10 s. Out of a total of 1211 independent reflections, 1066 were considered to be above zero at the 2σ significance level.

The structure was solved by direct methods.[10] Hydrogen atoms for the molecule of I were located from a difference map. Full-matrix least-squares refinement on positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogens gave final values of R and R_w of 0.043 and 0.042, respectively.[11] In this refinement, the reflections were weighted according to the scheme proposed by Corfield, Doedens, and Ibers.[12] The value of $[\Sigma w\Delta^2/(m - n)]^{1/2}$ was 2.59. The scattering curves for carbon and oxygen were those compiled by Cromer and Mann[13] and that for hydrogen is due to Stewart, Davidson, and Simpson.[14] The final atomic coordinates for I are listed in Table II; the final values for the thermal parameters and lists of h, k, l, $|F_o|$, $|F_c|$, and α_{calcd} are available as supplementary material (see paragraph at end of text regarding supplementary material). The coordinates, temperature factors, and phases presented are those corresponding to the enantiomer *R*-(−)-I rather than to the form *S*-(+)-I that was actually studied.

Crystals of racemic 2,2-diphenylcyclopropanecarboxylic acid were also obtained. The space group was established as $P2_1/c$ with a = 11.77, b = 9.48, c = 11.44 Å, and β = 113°. There are four molecules of the acid in the unit cell and the cell volume is 1175 Å^3.

Table II. Final Atomic Coordinates for I[a]

	x	y	z
C(1)	0.2378(2)	0.0720(8)	0.2169(4)
C(2)	0.2846(2)	0.2143[b])	0.1193(4)
C(3)	0.2577(3)	0.3078(9)	0.2619(5)
C(4)	0.3971(2)	0.1765(8)	0.1794(4)
C(5)	0.4333(3)	−0.0172(9)	0.1525(5)
C(6)	0.5360(3)	−0.0470(11)	0.1984(7)
C(7)	0.6036(3)	0.1150(15)	0.2747(6)
C(8)	0.5703(3)	0.3081(14)	0.3043(6)
C(9)	0.4670(3)	0.3445(9)	0.2576(5)
C(10)	0.2221(2)	0.2686(7)	−0.0870(4)
C(11)	0.2070(2)	0.1176(8)	−0.2232(4)
C(12)	0.1509(3)	0.1670(11)	−0.4142(5)
C(13)	0.1098(3)	0.3672(10)	−0.4698(6)
C(14)	0.1249(3)	0.5187(9)	−0.3361(7)
C(15)	0.1808(3)	0.4697(8)	−0.1455(6)
C(16)	0.1310(2)	−0.0027(8)	0.1177(4)
O(1)	0.0593(2)	0.1023(7)	0.0099(4)
O(2)	0.1210(2)	−0.2024(7)	0.1604(4)
H(1)	0.280(2)	−0.022(5)	0.302(4)
H(3a)	0.312(3)	0.357(8)	0.389(6)
H(3b)	0.195(2)	0.394(6)	0.227(4)
H(5)	0.393(3)	−0.134(6)	0.112(5)
H(6)	0.559(3)	−0.179(8)	0.184(6)
H(7)	0.679(3)	0.077(7)	0.309(5)
H(8)	0.611(4)	0.426(10)	0.355(7)
H(9)	0.439(3)	0.465(7)	0.287(5)
H(11)	0.237(3)	−0.024(7)	−0.193(5)
H(12)	0.145(3)	0.054(7)	−0.498(5)
H(13)	0.065(3)	0.421(8)	−0.619(6)
H(14)	0.097(3)	0.668(10)	−0.358(6)
H(15)	0.187(3)	0.564(7)	−0.052(5)
O(H)	0.052(3)	−0.252(8)	0.108(5)

[a] Hydrogen atoms are given the numbers of the atoms to which they are attached. [b] The y-coordinate of this atom was held constant to determine the origin in this direction.

X-Ray Structure Determination of *R*-(+)-2,2-Diphenyl-1-methylcyclopropanecarboxylic Acid (II). Crystal Data. $C_{17}H_{16}O_2$ has a molecular weight of 252.3: orthorhombic, a = 18.199(5), b = 6.309(1), c = 11.796(2) Å, V = 1354.4 Å^3, ρ_{obsd} = 1.231 g cm^{-3}, Z = 4, ρ_{calcd} = 1.24 g cm^{-3}, F(000) = 536, μ(Cu Kα) = 6.4 cm^{-1}. Systematic absences, h00 when $h = 2n + 1$, 0k0, when $k = 2n + 1$, and 00l when $l = 2n + 1$ established the space group as $P2_12_12_1$. Cell data were obtained by a least-squares fit to the settings for 10 hand-centered reflections (Cu Kα, λ 1.54178 Å).

Intensity data were collected as described in the previous section. Out of a total of 1364 reflections in the $2\theta \leq 130°$ sphere, 1261 were considered to be nonzero at the 2σ significance level. The structure was solved by direct methods.[10] Hydrogen atoms were positioned from a difference map. Full-matrix least-squares refinement of the positional and anisotropic thermal parameters for the non-hydrogen atoms and positional isotropic thermal parameters of the hydrogens gave final values for R and R_w of 0.037 and 0.038, respectively.[11] The weighting scheme and atomic scattering factors used were as described above. The value of $(\Sigma w\Delta^2/(m - n))^{1/2}$ was 2.52. The final atomic coordinates are listed in Table III; the final values for the thermal parameters and structure factors are available as supplementary material.

Table III. Final Atomic Coordinates for the Molecules of II[a]

	x	*y*	*z*
C(1)	0.67552(11)	0.3313(4)	0.2362(2)
C(2)	0.70163(12)	0.4573(4)	0.1310(2)
C(3)	0.68928(15)	0.5663(4)	0.2414(2)
C(4)	0.77981(2)	0.4258(4)	0.0909(2)
C(5)	0.80495(15)	0.2315(5)	0.0522(2)
C(6)	0.87511(17)	0.2113(6)	0.0083(3)
C(7)	0.92086(16)	0.3831(7)	0.0026(3)
C(8)	0.89662(15)	0.5764(6)	0.0395(3)
C(9)	0.82626(14)	0.5971(5)	0.0847(2)
C(10)	0.65034(12)	0.4965(4)	0.0332(2)
C(11)	0.63469(15)	0.3371(5)	−0.0430(2)
C(12)	0.59254(17)	0.3775(6)	−0.1387(3)
C(13)	0.56641(16)	0.5788(7)	−0.1593(3)
C(14)	0.58123(16)	0.7374(6)	−0.0832(3)
C(15)	0.62262(15)	0.6980(5)	0.0122(3)
C(16)	0.59693(13)	0.2684(4)	0.2360(2)
C(17)	0.72801(14)	0.1853(5)	0.2960(2)
O(1)	0.54586(9)	0.3871(3)	0.2223(2)
O(2)	0.58797(10)	0.0623(3)	0.2519(2)
H(3a)	0.7353(14)	0.607(4)	0.286(2)
H(3b)	0.6452(14)	0.650(4)	0.248(2)
H(5)	0.7740(17)	0.117(5)	0.056(3)
H(6)	0.8913(19)	0.073(6)	−0.017(3)
H(7)	0.9691(18)	0.375(5)	−0.028(3)
H(8)	0.9262(17)	0.694(5)	0.041(3)
H(9)	0.8088(16)	0.737(5)	0.116(2)
H(11)	0.6591(15)	0.200(5)	−0.036(2)
H(12)	0.5842(17)	0.261(5)	−0.193(3)
H(13)	0.5382(18)	0.603(5)	−0.228(3)
H(14)	0.5583(20)	0.881(6)	−0.096(3)
H(15)	0.6318(17)	0.812(5)	0.062(2)
H(17a)	0.7297(17)	0.043(6)	0.261(3)
H(17b)	0.7129(15)	0.171(5)	0.376(2)
H(17c)	0.7773(16)	0.243(4)	0.290(2)
O(H)	0.5427(21)	0.027(6)	0.260(3)

[a] Hydrogen atoms are given the number of the atom to which they are attached.

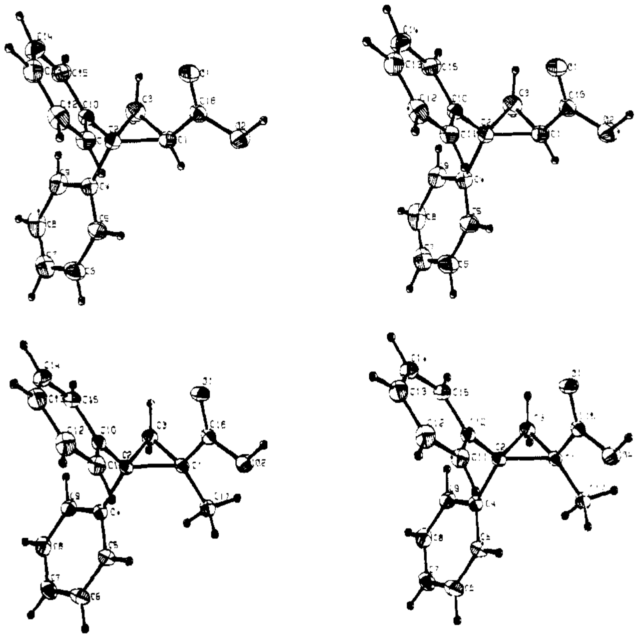


Figure 1. (Upper pair) Stereoscopic drawing of a single molecule of *R*-(−)-2,2-diphenylcyclopropanecarboxylic acid (I). (Lower pair) View of a single molecule of *R*(+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid (II).

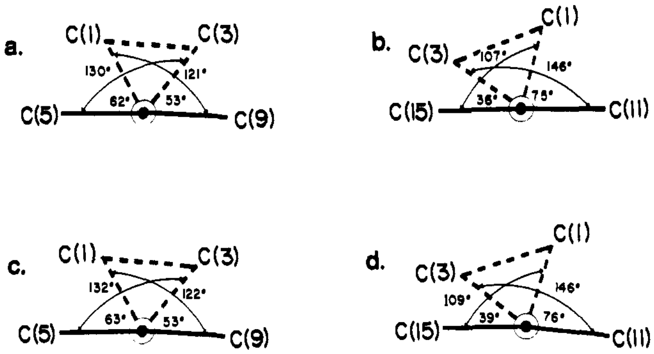


Figure 2. Views along the C(phenyl)-C(cyclopropane) bonds showing the torsion angles: (a) along the C(4)-C(2) bond in I, (b) along the C(10)-C(2) bond in I; (c) along the C(4)-C(2) bond in II; and (d) along the C(10)-C(2) bond in II.

Results and Discussion

Molecular Structure. Stereo drawings of single molecules of *R*-(−)-I and *R*-(+)-II (Figure 1) show that the molecular structures of the two cyclopropanecarboxylic acids are quite similar. Bond lengths and angles are listed in Table IV. The average C-C bond lengths are 1.379 ± 0.021 Å in ring C(4)-C(9) and 1.378 ± 0.011 Å in ring C(10)-C(15) for molecule I; the average C-C lengths are 1.379 ± 0.011 Å in ring C(4)-C(9) and 1.380 ± 0.007 Å in ring C(10)-C(15) for molecule II. The phenyl rings are oriented almost identically in the two molecules. The angles between the phenyl rings and various bonds in the cyclopropane ring when viewed along the C(phenyl)-C(cyclopropane) bonds are shown in Figure 2.

The variation of C-C bond lengths with exocyclic substituents in cyclopropane rings has been examined theoretically by Hoffmann[15] and some experimental results were described recently by Lauher and Ibers.[16] There is evidence for shortening of the C-C bond in the cyclopropane ring opposite a carbon to which is attached an unsaturated group. In addition to the examples given by Lauher and Ibers,[16] the effect is also shown in the structures of methyl-1-carbamoylcyclopropane-1-carboxylate[17] and three diterpenoids, barbatusin,[18] cyclobutatusin,[18] and dehydrocyclobutatusin.[19] In the present structures, the C-C bond, C(1)-C(2), opposite to the unsubstituted carbon in the cyclopropane ring is the longest among the C-C bonds in the ring; 1.533(5) and 1.548(3) Å in I and II, respectively. The fact that the C(2)-C(3) bond, opposite to the carboxyl group, is shorter than the C(1)-C(3) bond opposite to the phenyl-substituted carbon might be due to the bisecting orientation of the plane defined by the carboxyl group with respect to the plane defined by the cyclopropane ring. The bisecting orientation should favor conjugation between the π electrons of the unsaturated group and the C(2)-C(3) bent orbital of the cyclopropane ring, with consequent C-C bond shortening.[15] On the other hand, the two phenyl rings are in a less favorable position to overlap with the orbitals associated with the cyclopropane ring. The angles between the cyclopropane ring and the plane defined by the carboxyl group (C(16), O(1), O(2)) are 84 and 80° for I and II, while the angles that the C(1), C(2), C(3) plane makes with the two phenyl rings are 57 and 124° in I and 53 and 129° in II.

The carboxyl group adopts the syn-planar conformation usually found in crystals of carboxylic acids.[6] The two carbon-oxygen lengths in the carboxyl group are significantly different, 1.317(6) and 1.202(5) Å in I and 1.323(3) and 1.204(3) Å in II, with the hydrogen clearly bonded to O(2) in each case. The C-C-O angles are also considerably different; C(1)-C(16)-O(1) is 125.4(4)° while C(1)-C(16)-O(2) is 112.2(3)° in I, the corresponding values in II are 125.3(2) and 112.4(2)°. Investigation of a variety of aromatic carboxylic acids showed that there is a good linear correlation between Δr, the difference in the two C-O distances, and $\Delta\theta$, the dif-

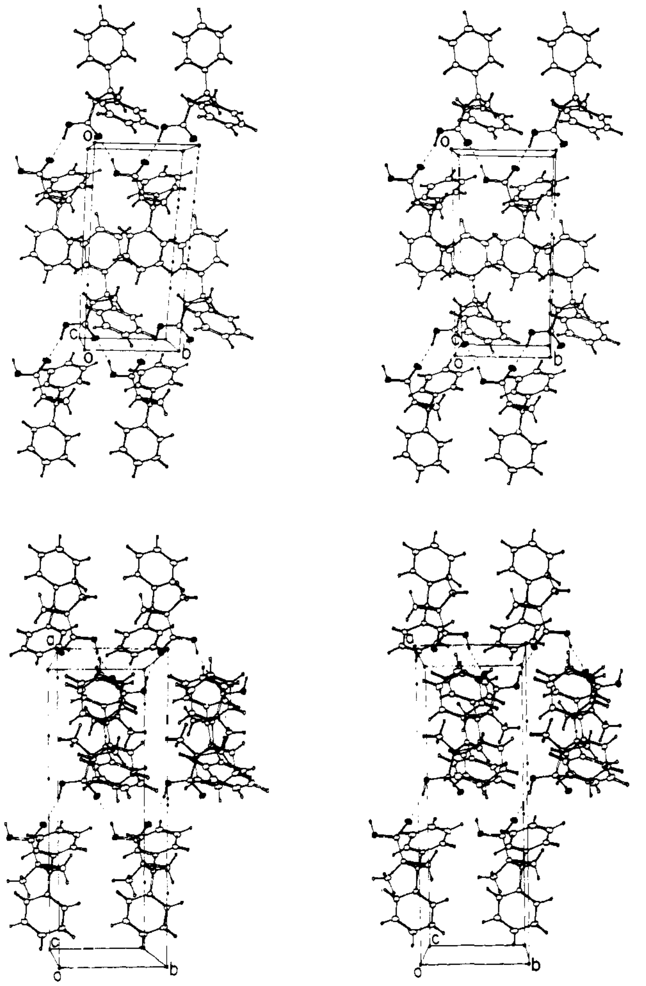


Figure 3. Stereoscopic views of the packing of I and II looking normal to the hydrogen-bonding chain. The oxygen atoms are shaded: (top) the packing of I; (bottom) the packing of II.

Table IV. Bond Lengths (Å) and Angles (deg) in I and II[a]

	I	II
C(1)-C(2)	1.533(5)	1.548(3)
C(1)-C(3)	1.510(7)	1.505(4)
C(2)-C(3)	1.481(5)	1.490(3)
C(2)-C(4)	1.511(4)	1.513(3)
C(4)-C(5)	1.376(7)	1.386(4)
C(5)-C(6)	1.389(6)	1.384(4)
C(6)-C(7)	1.350(10)	1.368(5)
C(7)-C(8)	1.361(12)	1.367(5)
C(4)-C(9)	1.397(7)	1.374(4)
C(8)-C(9)	1.402(7)	1.393(4)
C(2)-C(10)	1.509(4)	1.505(3)
C(10)-C(11)	1.376(6)	1.378(4)
C(11)-C(12)	1.393(5)	1.388(4)
C(12)-C(13)	1.369(9)	1.378(6)
C(13)-C(14)	1.364(6)	1.371(5)
C(10)-C(15)	1.378(7)	1.390(4)
C(14)-C(15)	1.390(7)	1.377(4)
C(1)-C(16)	1.470(5)	1.484(3)
C(16)-O(1)	1.202(5)	1.204(3)
C(16)-O(2)	1.317(6)	1.323(3)
C(1)-C(17)		1.503(4)
O(2)-H(O)	0.96(5)	0.86(4)
C(2)-C(1)-C(3)	58.3(2)	58.4(2)
C(2)-C(1)-C(16)	121.6(3)	115.6(2)
C(3)-C(1)-C(16)	118.6(4)	115.1(2)
C(1)-C(2)-C(3)	60.1(3)	59.3(2)
C(1)-C(2)-C(4)	115.2(2)	118.2(2)
C(1)-C(2)-C(10)	119.6(2)	120.6(2)
C(3)-C(2)-C(4)	116.9(3)	118.4(2)
C(3)-C(2)-C(10)	120.3(3)	120.1(2)
C(4)-C(2)-C(10)	114.2(2)	111.4(2)
C(1)-C(3)-C(2)	61.6(3)	62.3(2)
C(2)-C(4)-C(5)	122.1(3)	122.0(2)
C(2)-C(4)-C(9)	119.7(3)	119.5(2)
C(5)-C(4)-C(9)	118.2(4)	118.4(2)
C(4)-C(5)-C(6)	121.7(4)	120.6(3)
C(5)-C(6)-C(7)	120.1(5)	120.4(3)
C(6)-C(7)-C(8)	119.6(6)	119.6(3)
C(7)-C(8)-C(9)	121.8(6)	120.1(3)
C(4)-C(9)-C(8)	118.6(4)	120.8(3)
C(2)-C(10)-C(11)	120.3(3)	120.5(2)
C(2)-C(10)-C(15)	121.8(3)	120.8(2)
C(11)-C(10)-C(15)	118.0(4)	118.4(2)
C(10)-C(11)-C(12)	120.8(4)	120.7(3)
C(11)-C(12)-C(13)	120.5(4)	120.2(3)
C(12)-C(13)-C(14)	119.3(5)	119.3(3)
C(13)-C(14)-C(15)	120.3(5)	120.7(3)
C(10)-C(15)-C(14)	121.2(4)	120.6(3)
C(1)-C(16)-O(1)	125.4(4)	125.3(2)
C(1)-C(16)-O(2)	112.2(3)	112.4(2)
O(1)-C(16)-O(2)	122.4(4)	122.3(2)
C(2)-C(1)-C(17)		119.7(2)
C(3)-C(1)-C(17)		118.6(2)
C(16)-C(1)-C(17)		116.7(2)
C(16)-O(2)-H(O)	115(3)	113(3)

[a] The lengths of C-H bonds range from 0.90 to 1.11 Å.

ference between the two C-C-O angles.[20] In the present structures, the values of Δr and $\Delta\theta$ seem to follow the linear relationship found in the aromatic carboxylic acids. There seem to be no particular distortions elsewhere in the molecules.

Methyl-substituted cyclopropanes have been the subject of recent theoretical studies.[21,22] It has been suggested that the conformation of the methyl group in which one C-H bond bisects the small cyclopropane ring is favored rather than one where it straddles it.[22] The hydrogen atoms attached to the methyl carbon in II were found in well-defined positions and their arrangement seems to confirm the conclusion reached by Pople,[22] that one C-H bond bisects the C(2)-C(3) bond (Figure 1). A similar conclusion could be drawn from the results on dehydrocyclobutatusin.[19]

Crystal Packing. The most important feature of the packing in crystals of both I and II is hydrogen bonding. Stereoscopic drawings of the crystal packing viewed along the *c* axis in I and II are shown in Figure 3. In each case the long morphological axis is parallel to the direction of the hydrogen-bonded chains. The carbonyl oxygen of one molecule is involved as an acceptor from the hydroxyl hydrogen bond in an adjacent molecule related to the first molecule by the twofold screw along the *b* axis, while its hydroxyl group is hydrogen bonded to the carbonyl oxygen on the adjacent molecule on the other side, thus forming an infinite linear chain running parallel to the *b* axis. The type of linear hydrogen bonding found here had been proposed on the basis of IR studies.[7] The features of hydrogen bonding are almost identical in the two compounds I and II. The O---O distances are 2.651(4) and 2.692(3) Å in I and II while the O—H---O angles are 163.1(3) and 159.8(2)° and the C—O---O angles are 120.3(3) and 122.1(2)°, respectively, in I and II. In the two structures, the slightly longer O---O distance in II may account for the OH stretching band in the IR spectrum of II occurring at a slightly higher frequency (3200 cm^{-1} in I and 3230 cm^{-1} in II).[7] Similar linear hydrogen bonded chains have been found in the structures of a few other carboxylic acids. These have been summarized and factors affecting the choice between catemers and hydrogen-bonded dimers have been analyzed by Leiserowitz.[6] The present examples correspond to his motif (11b) which he calculated leads to translation axes of ~6.3 Å; this conclusion is in excellent agreement with our cell data. Pfeiffer[23] had shown earlier on the basis of powder x-ray data that (−)-I and (+)-II give rise to a solid solution of (−)-I in the (+)-II crystal structure and, in fact, this result had been used to support the determination of absolute configuration of I and II by Walborsky.[7] Our finding that the individual hydrogen-bonded chains of the molecules of resolved I and II are so similar supports the likelihood of such solid solution formation.

However, since I and II crystallize in different space groups, there are significant differences in packing. If the two rows of molecules parallel to the *b* axis held together by hydrogen bonding are considered to represent the linear chain, in I the sets of molecules associated with two adjacent hydrogen-bonded chains are related to each other by mere translations along the *a* axis, whereas in II they are related by a twofold screw along the *a* axis. As a result, the top two rows of molecules (Figure 3) in the two structures are in different orientations, i.e., the direction of orientation of the O═C-C-O-H groups in I along a hydrogen-bonded chain in an ideal single crystal is uniform (*b* is a polar axis in space group $P2_1$) while the directions of these groups in II alternate. In the crystal of I there are layers in the *bc* plane composed of C(4)-C(9) phenyl rings, without, however, overlap of the rings (Figures 3 and 4). The C(10)-C(15) rings effectively insulate the rows of carboxyl groups from each other in the *c* direction (Figure 4). The packing of molecules in II is more complex. In Figure 4 are shown views of the packing of both crystals looking along the *b* axis. The molecules of II that correspond to the packing of I are heavily outlined. A comparison of the two structures shows a remarkable similarity with the structure of II containing chains (coming out of the page in Figure 4) almost identical with those in I but these chains in II are interspersed with the addition of chains generated by the addition of twofold screw axis. From this it can be seen that the layers of C(4)-C(9) phenyl rings found in I are broken up by the chains of molecules running in the opposite direction. There are a number of contacts between methyl groups and phenyl rings. The net result of the packing of molecules of II is that the hydrogen-bonded chains are well insulated from each other by nonpolar groups. The packing coefficients,[24] 0.68 in I and 0.70 in II, suggest that the packing is slightly more efficient in II than in I; the melting point of II, 190-191°, is considerably higher than that of I, 150-151°.[9]

Reactions with Ammonia. The reaction of single crystals of I with ammonia gas was found to begin at the ends of the crystal and the reaction front thus formed migrated parallel to the *b* axis, that is, parallel to the direction of the hydrogen-bonded chains. The reaction is thus ditropic as was shown to be the case for II.[4] The explanation was previously advanced for the reaction of II[4] that as ammonia molecules react along *b* they create disorder in the structure which permits the access of additional ammonia molecules to further carboxyl groups along the hydrogen-bonded chain. On the other hand, progression of ammonia from one reactive carboxyl site to another along any path in the *ac* plane is impeded by the intervention of repeated hydrocarbon regions consisting of phenyl rings, methylene, and methyl groups. A similar argument applies to the reaction of I although both inspection of the structures (Figure 4) and examination of reacting crystals suggests that the somewhat looser packing of I makes reaction along *b* somewhat less favored than in the case of II. Since reaction along the two directions parallel to *b* of structure I constitutes reaction along a polar axis with significant structural differentiation in the two directions, it might be expected that the rate of reaction in the positive and negative directions along *b* in I would be different. Such a rate difference was observed along the polar axis in the reaction of *p*-bromobenzoic anhydride crystals with ammonia.[2] If there is an effect of the polar axis in the reaction of I, however, it is too small to be observed by the rather crude measurements of the rate of frontal migration we have employed.

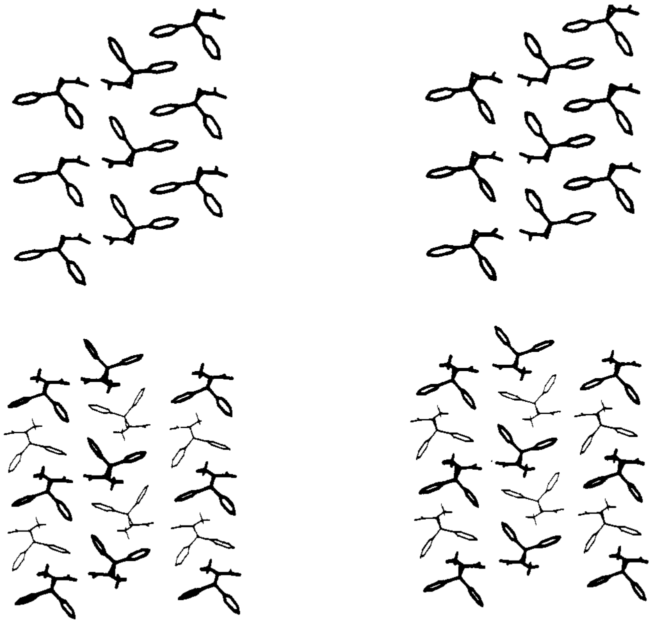


Figure 4. Views of the packing of I and II looking along the *b* axes: (top) the packing of I; (bottom) the packing of II. In the lower picture the molecules of II that have hydrogen bonds running in the same direction as those in the crystal of I are shown by heavier shading.

Reactions of Crystalline Acids I and II with Amines. Single crystals of I and II were found to react with gaseous methylamine, aniline, and α-phenylethylamine. (Photographs of the reaction of (+)-phenylethylamine with the acid I were published in a previous communication.[5]) None of these solid-gas reactions shows the specific reaction along the *b* axis shown by ammonia. Although there is evidence for anisotropic reaction of a different sort, the limited amount of work completed does not justify further discussion at this time.

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Supplementary Material Available: Final thermal parameters and observed and calculated structure factors for I and II (22 pages). Ordering information is available on any current masthead page.

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Ring-Closure Reactions. 9.[1] Kinetics of Ring Formation from *o*-*ω*-Bromoalkoxy Phenoxides and *o*-*ω*-Bromoalkyl Phenoxides in the Range of 11- to 24-Membered Rings. A Comparison with Related Cyclization Series[2]

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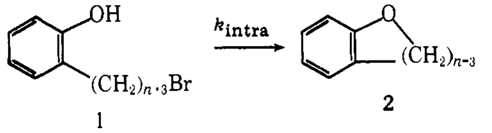
Abstract: Our quantitative investigations of the formation of aromatic mono- and diethers via intramolecular Williamson synthesis have been considerably extended. Kinetic data are now available for the 11-, 14-, and 16-membered monoethers and for the 11-, 12-, 13-, 14-, 16-, and 24-membered diethers. When combined with previous results, the present data provide a good insight into intramolecular reactivity, which spans seven powers of ten in the monoether series. Ring-closure reactivity is found to be remarkably insensitive to ring size in the large ring series, as a result of a substantial leveling off in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The influence of the oxygen atom on ease of ring closure has been shown to display a general decrease on decreasing the strain energy of the transition states. A striking feature emerges from a comparison of the reactivity data related to different cyclization reaction series, when brought out in terms of effective molarities (EM). Even though marked and significant structure-dependent differences are observed in the common- and medium-ring regions for several of the series considered, EM values converge to a rather narrow range of values between 0.1 and 0.01 M. This remarkable result suggests that the ease of formation of large rings is substantially independent of the nature of the functional groups, the length of the chain, and the presence of structural moieties other than methylene groups.

In the last few years a considerable interest has been devoted to intramolecular interactions of remote groups in long-chain compounds. A wealth of new information has been collected on chain length dependent phenomena also in fields other than mechanistic organic chemistry.[3-11]

Our studies[1] on ring-closure reactions of long-chain bifunctional substrates include the physical and mechanistic aspects of intra- vs. intermolecular reactivity and are intended to establish the relationship between structure and reactivity on a quantitative basis. A significant body of data is needed to allow an assessment of the ease of ring closure in terms of structure and size of the ring to be formed. Rate data and activation parameters in 75% aqueous ethanol have been reported for the formation of cyclic mono- and diethers, **2** and **4**,[12,13] up to ring size ten. We now report an extension of our kinetic studies to the formation of higher homologues in both series. Rate data have been obtained for the formation of the 11-, 14-, and 16-membered monoethers **2**, and of the 11-, 12-, 13-, 14-, 16-, and 24-membered diethers **4**. The activation parameters for representative terms in the diether series have also been determined.

When the results from the present work are compared with available quantitative data on large rings in related systems from this and other laboratories, a uniform pattern is revealed, which will be shown to be an inherent feature of large ring formation in general.



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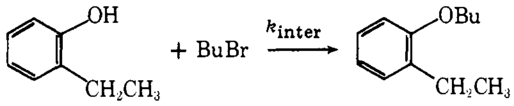

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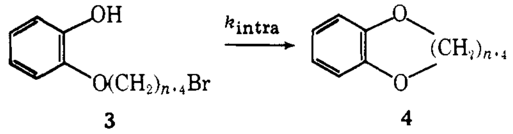
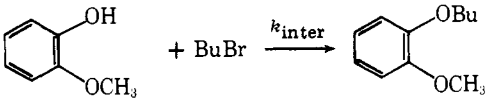


(2a)



(2b)

Experimental Section

Rate measurements and product analyses were carried out as previously described.[12,13] The preparation of the compounds used in this work has been reported elsewhere.[1]