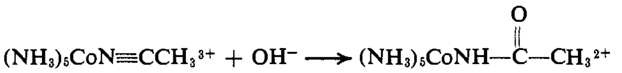
with H_2O in the solvent. Similar behavior has also been observed for protonation of $[Co(NH_3)_4(NH_2CH_2CONH)]^{2+}$,[13] and protonation of the carbonyl oxygen rather than the nitrogen atom is also claimed for uncoordinated acetamide.[14]

In the present case, some slow decomposition occurs in acidified DMSO with the liberation of free acetamide and the formation of $[Co(NH_3)_5(DMSO)]^{3+}$. The pmr signals associated with these products have not been included in Figure 2 for simplicity.

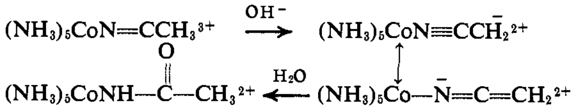
The pK_a of the protonated acetamide complex in aqueous solution is 3.02 (μ = 1.0 M, $NaClO_4$; T = 25°) which is slightly higher than those of the benzamide (pK_a = 1.65)[3] and formamide (pK_a = 2.16)[15] complexes of $Co(NH_3)_5{}^{3+}$, where protonation was indicated to be at the amide nitrogen atom. In view of the present work, it seems more likely that protonation will occur in these complexes at the carbonyl oxygen atom, and the pmr spectrum of the protonated benzamido complex in 1 M DCl solution confirms that there is only one proton at the nitrogen atom.

The rate law for the hydrolysis reaction is consistent with direct attack of hydroxide ion at the carbon atom of the nitrile group, giving rise to the acetamido complex, in the same way as proposed for the benzonitrile system.[3]



$$(NH_3)_5CoN{\equiv}CCH_3{}^{3+} + OH^- \longrightarrow (NH_3)_5CoNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3{}^{2+}$$

However, unlike the nitriles previously studied,[1-3] acetonitrile has hydrogen atoms on the carbon atom α to the cyano group. Pmr studies indicate that during the hydrolysis process, exchange of about half of the methyl protons occurs. (The rate of exchange of methyl protons in the acetamido complex is extremely slow.) Consequently, the rate of disappearance of the methyl signal of $[Co(NH_3)_5(N{\equiv}CCH_3)]^{3+}$ (k_{obsd} = 1.36 $\times$ 10^{-3} sec^{-1}) exceeds that of the hydrolysis (k_{obsd} = 9.7 $\times$ 10^{-4} sec^{-1}, measured spectrophotometrically) under the same conditions (Tris–$DClO_4$ buffer in D_2O, T = 33°, pD = 9.60) since in the former case both hydrolysis and exchange are observed. It is therefore possible that deprotonation may be a prerequisite to hydrolysis.



$$\begin{tikzcd}
(NH_3)_5CoN{\equiv}CCH_3{}^{3+} \arrow[r, "OH^-"] & (NH_3)_5CoN{\equiv}C\bar{C}H_2{}^{2+} \arrow[d, leftrightarrow] \\
(NH_3)_5CoNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3{}^{2+} & (NH_3)_5Co{-}\bar{N}{=}C{=}CH_2{}^{2+} \arrow[l, "H_2O"']
\end{tikzcd}$$

In the present instance, the rate of exchange is such that slightly more than one exchange occurs for every hydrolysis act. Alternatively, the two processes may be independent.

For the benzonitrile analog, similar studies reveal that exchange does not occur during hydrolysis so that no deprotonation of the phenyl protons is involved, presumably as no stabilization of the carbanion is possible. Thus, hydrolysis by direct attack of hydroxide ion on the nitrile carbon atom is most likely. The similarity in catalysis of the hydrolyses of benzonitrile and acetonitrile by $(NH_3)_5Co^{3+}$ (*ca.* 2 $\times$ 10^6) suggests some identity in the mechanisms, so that hydrolysis of acetonitrile in the pentaamminecobalt(III) complex would appear to occur by direct hydroxide attack also, with exchange being an independent process.

Acknowledgments. We are grateful to Dr. R. Bramley and Mr. C. Arandjelovic for assistance with the ^{14}N indor nmr spectra, and to the Microanalytical Unit for estimations of C, H, N, Co, and Cl.

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[13] D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **91**, 3451 (1969).

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The [8]Paracyclophane Ring System. Structure and Spectroscopic Properties of 4-Carboxy[8]paracyclophane[1-3]

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received March 1, 1973*

Abstract: An improved synthesis of 4-carboxy[8]paracyclophane is described. The nmr spectrum shows a highly shielded proton at δ −0.25. The X-ray crystal structure (R value 0.05 for 2187 unique nonzero maxima) shows that the molecule has normal bond lengths, but most of the C–C–C bond angles in the side chain are opened in an effort to bridge the ring. The ring is a boat, with the p carbons attached to the side chains 9° out of the plane of the other four ring carbons. There are many distances between atoms in the side chain and atoms in the ring which are less than the sum of the van der Waals radii.

Compounds having the [8]paracyclophane ring system have been known for some time.[4-7] These molecules are known from their ultraviolet spectra to possess a nonplanar benzene ring; however, in no case has the actual geometry of the benzene ring been re-

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[1] This work was supported in part by Grant AM-5836 from the National Institute of Arthritis and Metabolic Diseases.

[2] This is paper XCIV in the series "Conformational Analysis." Paper XCIII: C. J. Finder, M. G. Newton, and N. L. Allinger, *J. Chem. Soc., Perkin Trans. 2*, in press.

[3] Presented in part at the American Crystallographic Association Meeting, Gainesville, Fla., Jan 1973, Paper E9.

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[5] N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, **85**, 1171 (1963).

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[7] D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971).

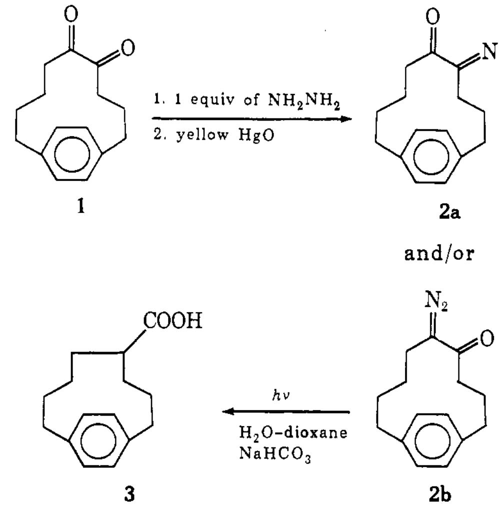
ported. Estimates of the degree of nonplanarity of the aromatic ring have been made from a comparison of experimental ultraviolet spectra with calculated values.[5] Since the spectral variations are not very large for small degrees of bending, the ring geometry can be determined in this way only approximately.

Considerable effort has been spent recently in developing force field methods for the calculation of structures of various kinds of organic molecules.[8] Aromatic compounds have so far not been dealt with in great detail.[9] In order to improve the force field for calculations concerning aromatic compounds, experimental data on deformed benzene rings would be highly desirable. While such data are available in profusion from compounds which contain two or more benzene rings,[7] such systems contain additional interactions not present in a compound containing only a single benzene ring. Experimental data are therefore desired on a few compounds containing a single benzene ring, which is deformed by steric constraints. The [8]paracyclophane ring system is one of this general category, and it was therefore judged worthwhile to study the system in detail, and in particular, to carry out a single crystal X-ray diffraction study of a suitable derivative (4-carboxy[8]paracyclophane) for the purpose of determining the exact structure.

The nmr spectra of some [8]paracyclophanes were reported earlier.[4-7] It was concluded that protons attached to the aliphatic chain that lie nearly above the aromatic ring were shielded by about 1 ppm. However, all reported nmr spectra were for molecules whose shielded protons were also affected by an adjacent deshielding group,[4] so a quantitative value for the shielding is not available.

An improved synthesis of 4-carboxy[8]paracyclophane is shown in Scheme I. The diketone (**1**) was prepared according to the method of Cram and Antar,[10] and was allowed to react with 1 equiv of 95% hydrazine to form the monohydrazone. The monohydrazone was not isolated, but was treated with yellow mercuric oxide at 0°, and then allowed to warm to room temperature with stirring for 8 hr. The resulting crude diazo ketone (**2a** and/or **2b**) was identified by its ir (Nujol): 2070 ($C{=}N_2$) and 1670 cm^{-1} ($C{=}O$). The crude diazo ketone was then photolyzed in an aqueous dioxane solution with suspended sodium bicarbonate for 12 hr. The resulting 4-carboxy[8]paracyclophane (**3**) was regularly isolated in 60–65% yield from the diketone.

Scheme I



After recrystallization from hexane, crystals suitable for X-ray study were obtained. The ir and uv were identical with that previously reported;[5] however, the melting point (84–85.5°) was slightly higher. The nmr [δ 11.8 (s, 1, COOH), 7.15 (m, 4, aromatic), 2.90 (m, 2, benzylic), 2.35 (m, 2, benzylic), 2.0–0.9 (m, 7, aliphatic protons), 0.9–0.4 (m, 3, partially shielded protons), −0.25 ppm (m, 1, highly shielded proton)] shows a previously unreported[5] proton signal at δ −0.25.

In **3**, there are hydrogens on C_5 (see Figure 1 for numbering system) over the benzene ring which are not deshielded by an adjacent group. From consideration of molecular models, the highly shielded proton at −0.25 ppm is clearly that attached to C_5. This represents a shielding of 1.6 ppm, which is larger than those reported in other [8]paracyclophane molecules.[4] This larger value may be in part due to the space demanding carboxyl group which restricts the inversion of the aliphatic chain. The methinyl proton on C_4, although strongly shielded by the aromatic ring, is deshielded by the carboxyl group and most likely lies in the multiplet between 0.9 and 0.4 ppm. These assignments are further supported by the results of the X-ray study.

The nmr spectrum of 4-carbomethoxy[8]paracyclophane (prepared from 4-carboxy[8]paracyclophane and diazomethane) is very similar to that of the 4-carboxy-[8]paracyclophane. The highly shielded C-5 proton again appears at −0.25 ppm. The partially shielded protons in the 0.9–0.4-ppm region are not clearly separated from the "normal" methylene protons.

Experimental Section

Physical Methods. Ir spectra were taken on a Perkin-Elmer, PE-257. A preliminary nmr spectrum was taken on a Varian T-60 without an internal reference. No protons were found in the region δ 4.3–5.3. Methylene chloride, δ 5.3, was then used as a lock and internal reference using the Varian HA-100. Chemical shifts are reported in parts per million from TMS. Mass spectra were recorded on a Hitachi Model RMU-6. Melting points were taken on an Elmer and Amend melting point block and are uncorrected. Analyses were by Atlantic Microlab, Inc., Atlanta, Ga.

4-Diazo-5-keto- and/or 4-Keto-5-diazo[9]paracyclophane (2a and/or 2b). To a round-bottom flask equipped with a stirrer was added 80 ml of purified *p*-dioxane,[11] 1.45 ml (1.46 g, 43.4 mmol) of 95+% hydrazine, and 10.0 g (43.4 mmol) of 4,5-diketo[9]paracyclophane.[10] The solution was heated at 100° with stirring for 12 hr, cooled, and then placed in an ice bath for 30 min, causing some of the monohydrazone to precipitate. Anhydrous ether (100 ml) and 10 g of anhydrous sodium sulfate were added with stirring. With continued cooling and stirring, 30.0 g (139 mmol) of yellow mercuric oxide was added, followed by 1.2 ml of a cold saturated alcoholic potassium hydroxide solution.[12] The solution was removed from the ice bath and stirred at room temperature for 8 hr. Only after the addition of alcoholic potassium hydroxide did metallic mercury *slowly* appear. The solution was filtered and a portion of the solvent was evaporated under a stream of nitrogen (until the ether was gone). Crude orange crystals, mp 90.5–93.5° (lit.[5] mp 70–80°), were obtained from the side of the flask. The ir

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[8] N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972), and references therein.

[9] (a) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968); C. F. Shieh, D. McNally, and R. H. Boyd, *Tetrahedron*, **25**, 3653 (1969); (b) A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, **94**, 5612 (1972); (c) N. L. Allinger and J. T. Sprague, *ibid.*, **95**, 3893 (1973).

[10] D. J. Cram and F. Antar, *J. Amer. Chem. Soc.*, **80**, 3109 (1958).

[11] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 333, Method a.

[12] Patterned after C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 496.

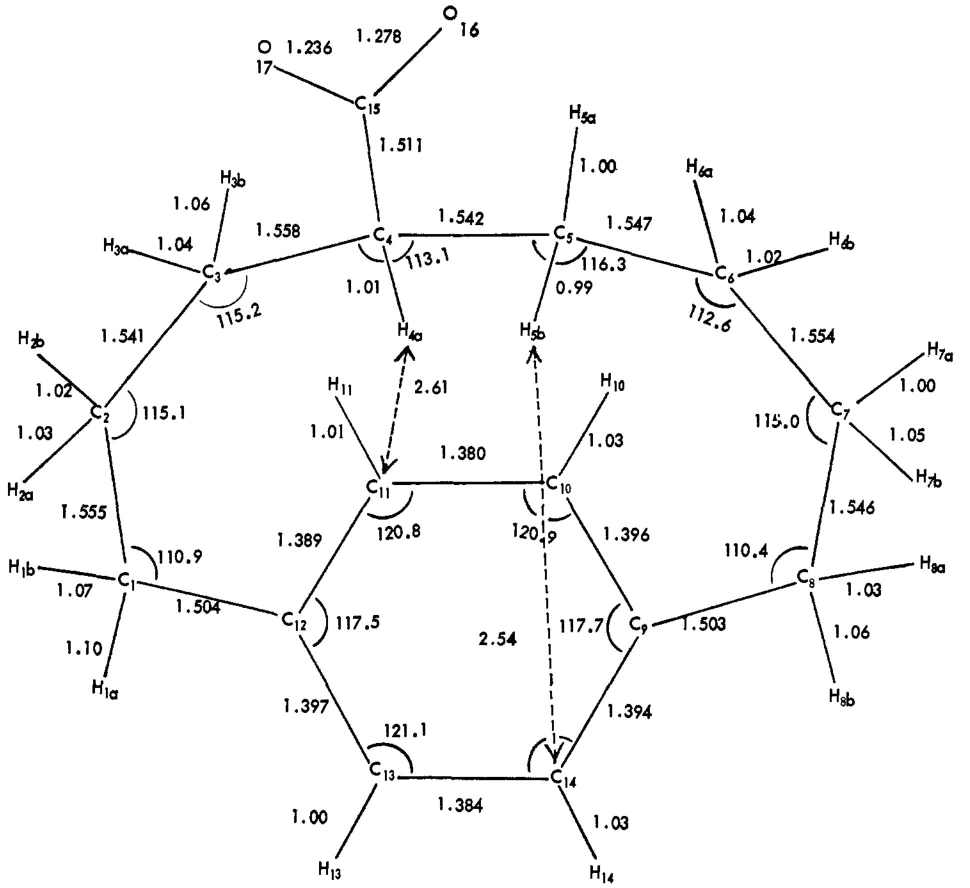

Figure 1. Numbering scheme for 4-carboxy[8]paracyclophane with selected bond lengths, bond angles, and interatomic distances.

(Nujol) [2070 ($C{=}N_2$) and 1670 cm^{-1} ($C{=}O$)] indicated the presence of the diazo ketone. No attempt was made to purify the diazo ketone.

4-Carboxy[8]paracyclophane (3). To a 1-l. Pyrex round-bottom flask was added the crude diazo ketone in the remaining *p*-dioxane from the previous step, 420 ml of purified *p*-dioxane,[11] 200 ml of water, and 7.2 g (86.8 mmol) of sodium bicarbonate. The stirred solution with the suspended bicarbonate was placed in an oil bath at 100° while being irradiated with a Sears 275 W sun lamp for 12 hr. Ether was added to the cooled solution and the layers were separated. The organic fraction was extracted twice with 10% sodium hydroxide. The aqueous extracts were acidified with hydrochloric acid and extracted with ether. The ether extracts were washed with water, washed with saturated salt solution, and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was recrystallized from ethanol and water to produce 6.59 g (65% from diketone 1) of 4-carboxy[8]paracyclophane. A portion was recrystallized from hexane to produce X-ray quality crystals: mp 84.0–85.5° (lit.[5] mp 80–81°); ir spectrum was the same as previously reported;[5] nmr (CCl_4) δ 11.8 (s, 1, COOH), 7.15 (m, 4, aromatic), 2.90 (m, 2, benzylic), 2.35 (m, 2, benzylic), 2.0–0.9 (m, 7, aliphatic protons), 0.9–0.4 (m, 3, partially shielded protons), and −0.25 ppm (m, 1, highly shielded proton); mass spectrum (70 eV) M$^+$ 232 (calcd 232); uv max (95% EtOH) 282 mm (ϵ 285), 275 (329), and 229 (7380).

4-Carbomethoxy[8]paracyclophane. To a solution of 5.0 g (21.5 mmol) of 4-carboxy[8]paracyclophane in 100 ml of ether was added an ether solution of alcohol-free diazomethane[13] until the yellow color persisted. The solution was allowed to stand for 1 hr at room temperature. The ether was evaporated and the remaining brownish oil was distilled to produce 4.7 g (89%) of clear oil: bp 131–133° (1.0 mm); ir (neat) 1735 ($C{=}O$) and 810 cm^{-1} (para-disubstituted benzene); nmr (CH_2Cl_2) δ 7.15 (m, 4, aromatic), 3.45 (s, 3, OCH_3), 2.9 (m, 2, benzylic), 2.35 (m, 2, benzylic), 2.0–0.4 (m, 10, aliphatic protons), and −0.25 ppm (m, 1, highly shielded proton). *Anal.* Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.98; H, 9.02.

X-Ray Structure Determination. Crystals of 4-carboxy[8]paracyclophane were grown in hexane. A crystalline sample suitable for collection of intensity data was cut from a larger needle crystal. Precession photographs revealed a monoclinic system mounted along the unique *b* axis, and systematic absences unambiguously identified the space group as $P2_1/c$. A summary of crystal data is provided in Table I.

Table I. Summary of Crystallographic Data

Molecular formula: $C_{15}H_{20}O_2$
Molecular weight: 232.31
Linear absorption coefficient, μ: 6.28 cm^{-1} (for Cu Kα)
Observed density (floatation in aqueous $ZnCl_2$): 1.21 g/cm^3
Calculated density: 1.21 g/cm^3 (assuming $Z = 4$)
Crystal dimensions: 0.6 × 0.2 × 0.2 mm
Space group: $P2_1/c$
Cell constants: a = 12.807 (3), b = 6.144 (1), c = 16.354 (4) Å, β = 98.07 (4)°

The crystal was transferred to an Enraf-Nonius CAD-4 diffractometer. The orientation matrix and cell dimensions were calculated using 13 accurately centered reflections near $\theta = 30°$. Intensity data were collected to a maximum θ of 75° using Cu Kα (λ 1.54180 Å) radiation and a graphite monochromator. In all, 2676 reflections were measured and recorded. Rejection of reflections less than $2\sigma(F_o)$ gave 2187 unique nonzero diffraction maxima which were used in solution and refinement of the structure.

The data were corrected for Lorentz polarization effects,[14] and reduced to an absolute scale by the method of Wilson[15] utilizing

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(13) Reference 11, pp 191–192, Method b.

(14) Corrections were made using program DATRED, a PL-1 program for the IBM 360: M. G. Newton and C. J. Finder, University of Georgia.

(15) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

Table II. Positional Coordinates and Temperature Factors[a] for 4-Carboxy[8]paracyclophane

Atom	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C_1	0.18595 (17)	0.43897 (40)	0.81233 (11)	0.00790 (14)	0.04280 (85)	0.003063 (68)	0.00443 (57)	0.00265 (16)	0.00500 (38)
C_2	0.10678 (15)	0.57509 (34)	0.75199 (11)	0.00697 (13)	0.03017 (65)	0.003407 (70)	0.00392 (47)	0.00311 (15)	0.00271 (34)
C_3	0.08302 (13)	0.48342 (31)	0.66362 (10)	0.00485 (10)	0.02565 (57)	0.003423 (66)	−0.00075 (38)	0.00151 (13)	0.00387 (31)
C_4	0.14942 (12)	0.58396 (28)	0.60017 (09)	0.00411 (09)	0.02286 (53)	0.002796 (58)	0.00015 (34)	0.00040 (11)	−0.00213 (26)
C_5	0.18709 (13)	0.41352 (31)	0.54154 (11)	0.00503 (10)	0.02560 (58)	0.003482 (67)	0.00203 (38)	0.00089 (13)	0.00095 (30)
C_6	0.28628 (15)	0.47379 (36)	0.50227 (11)	0.00605 (12)	0.03493 (71)	0.003480 (69)	0.00488 (47)	0.00252 (15)	0.00256 (36)
C_7	0.36108 (16)	0.27640 (40)	0.49728 (12)	0.00683 (13)	0.04138 (83)	0.003774 (77)	0.00822 (53)	0.00218 (16)	−0.00324 (41)
C_8	0.45125 (15)	0.25557 (41)	0.57036 (13)	0.00574 (12)	0.04290 (85)	0.004535 (86)	0.00843 (53)	0.00173 (16)	−0.00201 (44)
C_9	0.40889 (13)	0.27845 (33)	0.65113 (11)	0.00454 (10)	0.02995 (65)	0.003862 (72)	0.00441 (40)	−0.00012 (13)	0.00059 (34)
C_{10}	0.41755 (13)	0.47527 (33)	0.69435 (11)	0.00447 (10)	0.02920 (64)	0.003863 (70)	−0.00159 (39)	−0.00072 (13)	0.00084 (34)
C_{11}	0.35421 (14)	0.51911 (33)	0.75400 (10)	0.00581 (11)	0.02791 (62)	0.003130 (64)	−0.00013 (41)	−0.00119 (13)	0.00012 (32)
C_{12}	0.27886 (14)	0.37011 (34)	0.77157 (10)	0.00612 (12)	0.03126 (67)	0.002689 (61)	0.00207 (43)	0.00004 (14)	0.00403 (32)
C_{13}	0.28245 (15)	0.16136 (35)	0.73803 (12)	0.00672 (13)	0.02711 (65)	0.004420 (83)	0.00019 (46)	0.00052 (16)	0.00652 (37)
C_{14}	0.34694 (16)	0.11540 (33)	0.67905 (13)	0.00659 (13)	0.02529 (63)	0.004624 (84)	0.00384 (45)	−0.00036 (16)	0.00213 (37)
C_{15}	0.08980 (12)	0.77101 (29)	0.55528 (09)	0.00428 (09)	0.02308 (53)	0.002704 (55)	−0.00121 (34)	0.00070 (11)	0.00132 (27)
O_{16}	0.04348 (13)	0.90451 (25)	0.59820 (08)	0.01207 (14)	0.03302 (53)	0.003560 (55)	0.01617 (42)	0.00453 (14)	0.00330 (26)
O_{17}	0.08520 (13)	0.79509 (26)	0.47977 (08)	0.01198 (14)	0.03643 (55)	0.002907 (49)	0.01594 (43)	0.00291 (13)	0.00445 (26)
H_{1a}	0.1443 (16)	0.2963 (35)	0.8306 (12)	3.11 (46)					
H_{1b}	0.2143 (19)	0.5336 (43)	0.8659 (14)	5.00 (61)					
H_{2a}	0.0364 (15)	0.5857 (33)	0.7761 (11)	2.44 (42)					
H_{2b}	0.1359 (16)	0.7296 (35)	0.7529 (12)	2.90 (44)					
H_{3a}	0.0940 (14)	0.3159 (33)	0.6636 (12)	2.23 (39)					
H_{3b}	0.0020 (13)	0.5014 (30)	0.6413 (10)	1.68 (36)					
H_{4a}	0.2164 (13)	0.6497 (30)	0.6305 (10)	1.46 (35)					
H_{5a}	0.1267 (14)	0.3734 (31)	0.4981 (11)	1.96 (38)					
H_{5b}	0.2031 (15)	0.2797 (33)	0.5743 (11)	2.33 (40)					
H_{6a}	0.2673 (16)	0.5281 (36)	0.4418 (12)	3.02 (46)					
H_{6b}	0.3250 (17)	0.5937 (37)	0.5375 (13)	3.65 (51)					
H_{7a}	0.3960 (16)	0.2811 (37)	0.4460 (13)	3.21 (46)					
H_{7b}	0.3179 (17)	0.1313 (39)	0.4909 (13)	4.00 (54)					
H_{8a}	0.4932 (18)	0.1155 (40)	0.5632 (14)	4.16 (54)					
H_{8b}	0.5101 (18)	0.3711 (39)	0.5614 (14)	3.91 (52)					
H_{10}	0.4634 (15)	0.6016 (33)	0.6787 (11)	2.58 (43)					
H_{11}	0.3598 (15)	0.6666 (34)	0.7817 (11)	2.60 (42)					
H_{13}	0.2311 (17)	0.0561 (38)	0.7566 (13)	3.64 (50)					
H_{14}	0.3449 (17)	−0.0306 (37)	0.6479 (12)	3.68 (50)					

[a] Anisotropic temperature factors (β_{ij}) have the form $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

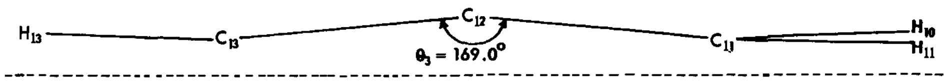

Figure 2. View of the benzene ring distortion looking down the C_{10}–C_{11} and C_{13}–C_{14} bonds in 4-carboxy[8]paracyclophane.

the computer program FAME.[16] Application of the symbolic addition procedure using the 278 E values greater than 1.50 produced consistent phases for all but 25 of the starting set. These phased values produced an E map[17] which gave starting positions for all carbon and oxygen atoms. A structure factor calculation using these atomic positions gave an initial conventional R value of 0.358. Isotropic refinement[18] of the carbon and oxygen skeleton using unit weights reduced the R value to 0.165. Anisotropic refinement employing weights of $1/\sigma(F_o)$[19] gave an unweighted R value of 0.103. A difference Fourier utilizing data from the anisotropic refinement gave starting positions for 19 of the 20 hydrogen atoms. The carboxylic hydrogen could not be located. The hydrogen atomic positions and isotropic temperature factors were refined while holding carbon and oxygen atom parameters constant, reducing R to 0.062. Refinement of the carbon and oxygen skeleton reduced R to 0.052. One final refinement of hydrogen positions and B's gave the final R of 0.051.[20] No peaks larger than 0.2 e Å^{-3} were found in a final difference map and none of these were in chemically meaningful positions. Table II contains values of final atomic parameters and temperature factors with estimated standard deviations of each value given in parentheses.

Figure 1 shows the numbering scheme of a molecule and selected bond lengths and angles.

Results and Discussion

Bond distances and estimated standard deviations are listed in Table III. No bond distances are significantly different from values usually associated with the various bond types. C_{sp^3}–C_{sp^3} distances in the 8-carbon bridge average 1.549 Å. The C_1–C_{12} and C_8–C_9 distances of 1.504 and 1.503 Å are normal for aromatic C_{sp^2}–C_{sp^3} bonds. Aromatic C–C bonds average 1.390 Å. Bridge C–H bonds average 1.03 A; aromatic C–H distances average 1.02 Å.[21]

Values similar to the carboxylic acid C–O distances of 1.236 and 1.278 Å have been observed in recent structure determinations of *cis*-1,2-cyclobutanedicarboxylic acid,[22] *cis*-4-*tert*-butylcyclohexanecarboxylic acid,[23] and *trans*-cyclohexanedicarboxylic acid.[24] These C–O lengths are significantly different from distances observed in many carboxylic acids where C═O and C—OH are about 1.21 and 1.31 Å, respectively.[25] Since a 1:1 positional disorder would require equal C–O lengths, there must exist only a partial disorder of the acidic hydrogen.[22] This idea is supported in the present study by the fact that the carboxylic hydrogen could not be located from the final difference Fourier synthesis.

Bond angles are shown in Table IV. The aromatic

Table III. Bond Distances between Bound Atoms

Atoms	Distance, Å^a	Atoms	Distance, Å^a
C_1–C_2	1.555 (3)	C_1–H_{1a}	1.09 (2)
C_1–C_{12}	1.504 (3)	C_1–H_{1b}	1.07 (2)
C_2–C_3	1.541 (3)	C_2–H_{2a}	1.04 (2)
C_3–C_4	1.558 (2)	C_2–H_{2b}	1.02 (2)
C_4–C_5	1.542 (2)	C_3–H_{3a}	1.04 (2)
C_4–C_{15}	1.511 (2)	C_3–H_{3b}	1.06 (2)
C_5–C_6	1.547 (3)	C_4–H_{4a}	1.01 (2)
C_6–C_7	1.554 (3)	C_5–H_{5a}	1.00 (2)
C_7–C_8	1.546 (3)	C_5–H_{5b}	0.99 (2)
C_8–C_9	1.503 (3)	C_6–H_{6a}	1.04 (2)
C_9–C_{10}	1.396 (3)	C_6–H_{6b}	1.02 (2)
C_9–C_{14}	1.394 (3)	C_7–H_{7a}	1.00 (2)
C_{10}–C_{11}	1.380 (3)	C_7–H_{7b}	1.05 (2)
C_{11}–C_{12}	1.389 (3)	C_8–H_{8a}	1.03 (2)
C_{12}–C_{13}	1.397 (3)	C_8–H_{8b}	1.06 (2)
C_{13}–C_{14}	1.384 (3)	C_{10}–H_{10}	1.03 (2)
C_{15}–O_{16}	1.278 (2)	C_{11}–H_{11}	1.01 (2)
C_{15}–O_{17}	1.236 (2)	C_{13}–H_{13}	1.00 (2)
		C_{14}–C_{14}	1.03 (2)

[a] The estimated standard deviations given in parentheses do not contain cell constant errors and have not been corrected for thermal motion.

Table IV. Bond Angles between Bound Atoms

Atoms	Angle, deg	Atoms	Angle, deg
C_2–C_1–C_{12}	110.9 (2)	C_4–C_3–C_{3a}	108 (1)
C_1–C_2–C_3	115.1 (2)	C_4–C_3–H_{3b}	109 (1)
C_2–C_3–C_4	115.2 (2)	H_{3a}–C_3–H_{3b}	103 (1)
C_3–C_4–C_5	113.1 (1)	C_3–C_4–C_{4a}	110 (1)
C_3–C_4–C_{15}	109.8 (1)	C_5–C_4–C_{4a}	105 (1)
C_5–C_4–C_{15}	113.3 (1)	C_{15}–C_4–C_{4a}	106 (1)
C_4–C_5–C_6	116.3 (2)	C_4–C_5–H_{5a}	109 (1)
C_5–C_6–C_7	112.6 (2)	C_4–C_5–H_{5b}	107 (1)
C_6–C_7–C_8	115.0 (2)	C_6–C_5–H_{5a}	111 (1)
C_7–C_8–C_9	110.4 (2)	C_6–C_5–H_{5b}	108 (1)
C_8–C_9–C_{10}	120.8 (2)	H_{5a}–C_5–H_{5b}	105 (2)
C_8–C_9–C_{14}	120.9 (2)	C_5–C_6–H_{6a}	112 (1)
C_{10}–C_9–C_{14}	117.7 (2)	C_5–C_6–H_{6b}	108 (1)
C_9–C_{10}–C_{11}	120.9 (2)	C_7–C_6–H_{6a}	105 (1)
C_{10}–C_{11}–C_{12}	120.8 (2)	C_7–C_6–H_{6b}	110 (1)
C_1–C_{12}–C_{11}	121.5 (2)	H_{6a}–C_6–H_{6b}	110 (2)
C_1–C_{12}–C_{13}	120.2 (2)	C_6–C_7–H_{7a}	112 (1)
C_{11}–C_{12}–C_{13}	117.5 (2)	C_6–C_7–H_{7b}	110 (1)
C_{12}–C_{13}–C_{14}	121.1 (2)	C_8–C_7–H_{7a}	106 (1)
C_9–C_{14}–C_{13}	120.3 (2)	C_8–C_7–H_{7b}	110 (1)
C_4–C_{15}–O_{16}	117.6 (1)	H_{7a}–C_7–H_{7b}	104 (2)
C_4–C_{15}–O_{17}	121.7 (2)	C_7–C_8–H_{8a}	109 (1)
O_{16}–C_{15}–O_{17}	120.7 (2)	C_7–C_8–H_{8b}	108 (1)
C_2–C_1–H_{1a}	108 (1)	C_9–C_8–H_{8a}	116 (1)
C_2–C_1–H_{1b}	110 (1)	C_9–C_8–H_{8b}	114 (1)
C_{12}–C_1–H_{1a}	110 (1)	H_{8a}–C_8–H_{8b}	99 (2)
C_{12}–C_1–H_{1b}	109 (1)	C_9–C_{10}–H_{10}	122 (1)
H_{1a}–C_1–H_{1b}	110 (2)	C_{11}–C_{10}–H_{10}	116 (1)
C_1–C_2–H_{2a}	109 (1)	C_{10}–C_{11}–H_{11}	119 (1)
C_1–C_2–H_{2b}	107 (1)	C_{12}–C_{11}–H_{11}	120 (1)
C_3–C_2–H_{2a}	108 (1)	C_{12}–C_{13}–H_{13}	115 (1)
C_3–C_2–H_{2b}	112 (1)	C_{14}–C_{13}–H_{13}	124 (1)
H_{2a}–C_2–H_{2b}	106 (2)	C_9–C_{14}–H_{14}	116 (1)
C_2–C_3–H_{3a}	111 (1)	C_{13}–C_{14}–H_{14}	123 (1)
C_2–C_3–H_{3b}	110 (1)		

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(16) The computer programs FAME, MAGIC, LINK, and SYMPL used in the symbolic addition procedure for centric space groups were written by R. A. Dewar, A. Stone, and E. B. Fleischer, The University of Chicago, Chicago, Ill.

(17) The Fourier program used is FORDAP, written by A. Zalkin, Lawrence Radiation Lab, Livermore, Calif.

(18) The full-matrix, least-squares program (UCLALS) used in refinement was written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood and modified by M. G. Newton for IBM 360.

(19) The standard deviation of F_{hkl}, $\sigma(F_o)$, is obtained from counting statistics and is computed by

$$\sigma(F_o) = \frac{1}{2\sqrt{L_p}}\sqrt{\frac{(at + 1)I + 4(B_l + B_r) + (\varkappa I_r)^2}{s(I - 2)(B_l + B_r)}}$$

where I = total measured peak intensity + backgrounds, B_l = left background, B_r = right background, $I_r = \{(at + 1)/s\}I - 2(B_l + B_r)$, s = scan speed for the measurement, t = attenuation filter (t = 1 if filter was used in the measurement, t = 0 if no filter was included), a = attenuation filter factor = 25.5, $\varkappa$ = standard deviation for instrumental instability (the value of $\varkappa$ is estimated from control reflections), L_p = Lorentz-polarization correction.

(20) See paragraph at end of paper regarding supplementary material.

(21) C–H distances measured by X-ray analyses are normally shorter than those measured by electron diffraction or microwave studies. See "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 276.

(22) D. van der Helm, I. Hsu, and J. M. Sims, *Acta Crystallogr., Sect. B*, **28**, 3109 (1972).

(23) H. van Koningsveld, *Acta Crystallogr., Sect. B*, **28**, 1189 (1972).

(24) V. P. Luger, K. Plieth, and G. Ruban, *Acta Crystallogr., Sect. B*, **28**, 706 (1972).

(25) For a recent example, see H. Hope and U. de la Camp, *Acta Crystallogr., Sect. A*, **28**, 201 (1972).

Figure 3. Distortion of the benzene ring from planarity in 4-carboxy[8]paracyclophane.

C–C–C angles are not significantly different from 120° with the exception of the carbon atoms attached to the [8] bridge. The decrease in the C_{10}–C_9–C_{14} and C_{11}–C_{12}–C_{13} angles to 117.7 and 117.4° is characteristic of all the paracyclophanes.[26]

Examination of the nonbonded interatomic distances between bridge hydrogens and atoms of the aromatic ring reveals several distances which are less than the sum of the van der Waals radii[8] (see Table V). This suggests that no completely suitable, noninteracting positions are available to these hydrogens. The result of these repulsions is the significant distortion of angles in the bridge and the planarity of the benzene ring.

Table V. Intramolecular Nonbonded C–H Distances

Atoms	Distance, Å[a]	Atoms	Distance, Å[a]
H_{4a}–C_{11}	2.61 (2)*	H_{5b}–C_{14}	2.54 (2)*
H_{4a}–C_{12}	2.90 (2)*	H_{5b}–C_9	2.76 (2)*
H_{4a}–C_{13}	3.52 (2)	H_{5b}–C_{10}	3.37 (2)
H_{4a}–C_{14}	3.72 (2)	H_{5b}–C_{11}	3.60 (2)
H_{4a}–C_9	3.34 (2)*	H_{5b}–C_{12}	3.28 (2)*
H_{4a}–C_{10}	2.85 (2)*	H_{5b}–C_{13}	2.82 (2)*
H_{4a}–H_{11}	2.87 (2)*	H_{5b}–H_{14}	2.79 (2)
H_{4a}–H_{10}	3.17 (2)	H_{5b}–H_{13}	3.25 (2)

[a] Distances marked with an asterisk are less than the sum of the van der Waals radii, using C_{sp^2}–H = 3.35 Å, and H–H = 3.0 Å.[8]

The C_{12}–C_1–C_2 and C_7–C_8–C_9 angles of 110.9 and 110.4° are significantly different from other C_{sp^3} angles in the 8-carbon bridge. These angles are smaller by about 4° than the average of the other bridging carbon angles. This contracted angle allows a more favorable approach to the benzene ring junction. The average C–C–C angle of the bridge atoms C_2 through C_7 is 114.5°. These values are larger than those observed for propane (112.4)[27] and simple alkanes (113.5).[28]

Table VI. Comparison of Nonbonded Distances between Benzene Ring Carbon Atoms and Bridge Carbon Atoms

	C_1	C_8	C_2	C_7	C_3	C_6	C_4	C_5
C_{10}	3.765 (2)	2.522 (3)	4.262 (2)	3.427 (3)	4.244 (2)	3.348 (3)	3.623 (2)	3.610 (2)
C_{13}	2.516 (3)	3.767 (3)	3.422 (3)	4.257 (3)	3.323 (3)	4.312 (3)	3.693 (3)	3.622 (3)
C_{14}	3.770 (3)	3.520 (3)	4.459 (3)	3.161 (3)	4.045 (2)	3.629 (3)	3.927 (3)	3.362 (3)
C_{11}	2.525 (3)	3.771 (3)	3.183 (2)	4.467 (3)	3.585 (2)	4.095 (3)	3.393 (2)	3.871 (2)

As observed in other strained cyclophanes, the benzene ring is not planar. Figure 3 shows the ring to be a shallow boat with C_9 and C_{12} out of the C_{10}–C_{11}–C_{13}–C_{14} plane by 0.11 Å; C_1 and C_8 deviate from the same plane by 0.58 and 0.55 Å, respectively. The average θ_1 angle is 9.1° and the average θ_2 angle is 7.8°. These values are smaller than those found in [2.2]metaparacyclophane-1,9-diene (θ_1 = 18.4, θ_2 = 18.0°),[29] [2.2]paracyclophane-1,9-diene (θ_1 = 13.5, θ_2 = 15),[26] [2.2]paracyclophane (θ_1 = 12.6, θ_2 = 11.2),[30] or [2.2]metaparacyclophane (θ_1 = 14, θ_2 = 14).[7] Corresponding values of [3.3]paracyclophane[26] are θ_1 = 6.4, θ_2 = 3.6.

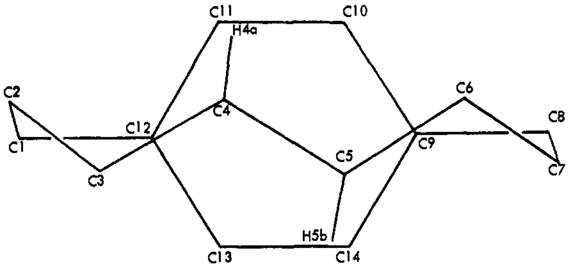

Figure 4. Projection of 4-carboxy[8]paracyclophane looking down the "C_2 axis" (from the midpoint of the C_4–C_5 bond to the center of the benzene ring). The figure is drawn to scale. The carboxyl group and most of the hydrogens are omitted for clarity.

Figure 2 shows a profile of the molecule viewed down the C_{10}–C_{11} and C_{13}–C_{14} bonds of the benzene ring. The folding angle, θ_3, between planes C_9–C_{10}–C_{11}–C_{12} and C_{12}–C_{13}–C_{14}–C_9 is 169.0°. Aromatic hydrogen atoms do not significantly deviate from the C_{10}–C_{11}–C_{13}–C_{14} plane. However, H_{10} and H_{11} are out of the C_9–C_{10}–C_{11}–C_{12} plane by 0.14 and 0.05 Å, respectively. Similarly, H_{13} and H_{14} are out of the C_{12}–C_{13}–C_{14}–C_9 plane by 0.09 and 0.12 Å, respectively. A similar but more dramatic effect was noted in [2.2]paracyclophane-1,9-diene.[31]

The parent hydrocarbon has only one possible conformation as predicted from *a priori* considerations of molecular models. That conformation possesses C_2 symmetry. From the structure study, we find that the acid derivative closely approximates this point symmetry if the carboxyl group is ignored in the considerations. Figure 4 illustrates this C_2 symmetry in a view of the molecule looking down a vector passing through the midpoint of the C_4–C_5 bond and the center of the benzene ring. Table VI shows pairwise comparisons of the 32 nonbonded distances between bridge carbon atoms and benzene ring carbon atoms. By comparing distances related diagonally in each block of the table, it is obvious that nonbonded distances of one-half the molecule closely match those of the opposite half. These comparisons are indicative of C_2 symmetry. The largest discrepancy (0.08 Å) occurs with C_4–C_{13} and C_5–C_{10} comparisons; this is not surprising since C_4 holds the carboxyl group. The symmetry of the molecule is also illustrated in the dihedral angles of the bridge carbon atoms shown in Table VII. These di-

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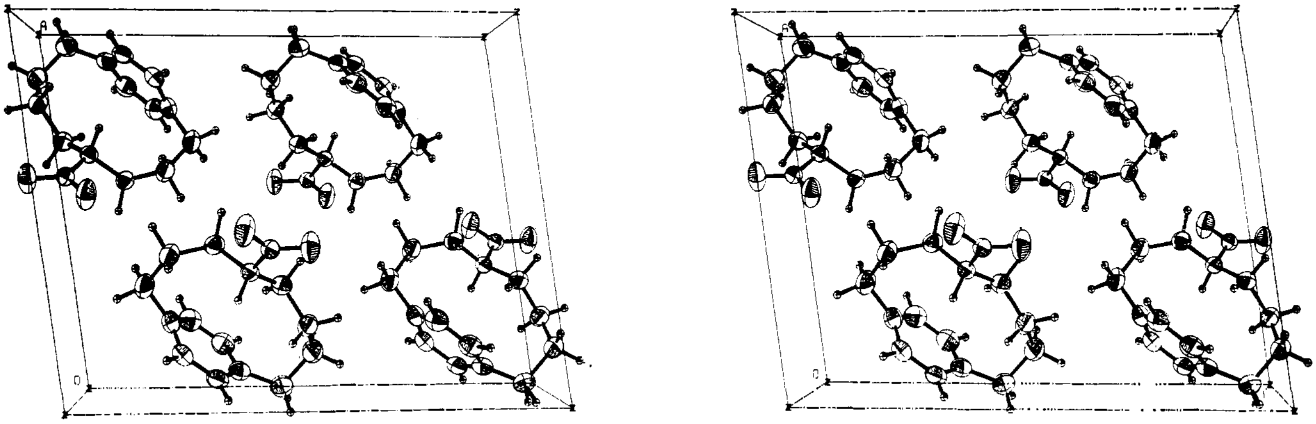

Figure 5. Unit cell packing drawing for 4-carboxy[8]paracyclophane (origin has been shifted to $x + {}^1/_2, y, z + {}^1/_2$).

Table VII. Pertinent Dihedral Angles in the 8-Carbon Bridge

Atoms (I-J-K-L)[a]	Angle, deg
C_2–C_1–C_{12}–C_{13}	−98.5 (2)
C_2–C_1–C_{12}–C_{11}	70.9 (2)
C_{12}–C_1–C_2–C_3	44.4 (2)
C_1–C_2–C_3–C_4	−96.1 (2)
C_2–C_3–C_4–C_5	138.8 (2)
C_3–C_4–C_5–C_6	−156.1 (2)
C_4–C_5–C_6–C_7	140.7 (2)
C_5–C_6–C_7–C_8	−94.5 (2)
C_6–C_7–C_8–C_9	48.0 (2)
C_7–C_8–C_9–C_{14}	70.8 (2)
C_7–C_8–C_9–C_{10}	−99.9 (2)

[a] The dihedral angle has a positive sign if vector K–L is clockwise from vector J–I when viewed down vector J–K, and a negative sign if counterclockwise.

hedral angle values are consistent in both magnitude and sign with approximate C_2 symmetry.

An ORTEP[32] drawing of the molecular packing in one unit cell is shown in Figure 5. The molecules form racemic carboxylic acid dimers occupying a crystallographic inversion center. The $O_{16}\cdots O_{17}$ intermolecular distance of 2.675 (2) Å is similar to corresponding contact distances in other recent carboxylic acid structures.[22-25] Table VIII lists those intermolecular distances that are less than 3.0 Å for C···H or O···H contacts and less than 2.7 Å for H···H contacts. Contact distances less than these values are assumed to be in the repulsive range of van der Waals forces. The closest approach between a heavy atom (C, O) and hydrogen is 2.664 Å ($O_{16}\cdots H_{2a}$). The H···H approach distance between H_{13} and H_{2b} of 2.343 is unusually short.

Table VIII. Intermolecular Contact Distances

Atom	Pair	Distance	Operation[b]
C, O, and H Contacts Less Than 3.0 Å[a]			
C_7	H_{8b}	2.96 (2)	III
C_{15}	H_{5a}	2.93 (2)	II
O_{16}	H_{1a}	2.89 (2)	IV
O_{16}	H_{2a}	2.66 (2)	IV
O_{16}	H_{3a}	2.78 (2)	I
O_{17}	H_{1b}	2.86 (2)	V
O_{17}	H_{3b}	2.80 (2)	II
O_{17}	H_{5a}	2.97 (2)	II
H–H Contacts Less Than 2.7 Å[a]			
H_{3a}	H_{2a}	2.49 (3)	IV
H_{3b}	H_{1a}	2.69 (3)	VII
H_{7b}	H_{1b}	2.49 (3)	VIII
H_{8a}	H_{8a}	2.53 (3)	VI
H_{8b}	H_{7a}	2.46 (3)	III
H_{8b}	H_{8b}	2.54 (3)	III
H_{13}	H_{2b}	2.34 (3)	I
H_{14}	H_{4a}	2.55 (3)	I

[a] Approach distances between C···H or O···H less than 3.0 Å are assumed to be in the repulsive range of van der Waals forces; the corresponding distance for H–H is assumed to be 2.7 Å. [b] Operations that relate a symmetry equivalent molecule to the original (coordinates in Table I) are: (I) $x, -1 + y, z$; (II) $-x, 1 - y, 1 - z$; (III) $1 - x, 1 - y, 1 - z$; (IV) $-x, -{}^1/_2 + y, 1{}^1/_2 - z$; (V) $x, 1{}^1/_2 - y, 1{}^1/_2 + z$; (VI) $1 - x, -y, 1 - z$; (VII) $-x, {}^1/_2 + y, 1{}^1/_2 - z$; (VIII) $x, {}^1/_2 - y, -{}^1/_2 + z$.

Supplementary Material Available. Listings of h, k, l, F_o, and F_c will appear following these pages in the microfilm edition of the volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105× 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5652.

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(32) ORTEP II, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations: C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37831.