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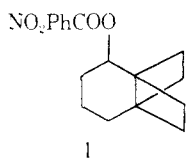
Structures of the [*n*. 2.2]Propellanes. I. 2-Hydroxy[4.2.2]propellane *p*-Nitrobenzoate

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Abstract: The complete crystal structure of the *p*-nitrobenzoate of 2-hydroxytricyclo[4.2.2.0^{1,4}]dodecane has been determined. The bond common to all three rings of this [4.2.2]propellane is longer (1.578 Å) than is normal for a bond between sp³-hybridized carbon atoms, and there is considerable angular distortion from tetrahedral values at the bridgehead atoms. The observed geometry and molecular orbital calculations indicate a greater than normal admixture of p-type orbitals in the bridgehead bond. Crystal data: $P2_1/n$, $a = 10.976$ (1), $b = 7.135$ (1), $c = 19.740$ (1) Å; $\beta = 90.43$ (1)°; $Z = 4$; $d_x = 1.294$ g cm⁻³; $d_m = 1.28$ (1) g cm⁻³; Cu K α radiation (λ 1.5418 Å). The structure was solved by direct methods using counter-measured X-ray intensity data (max sin $\theta/\lambda = 0.61$ Å⁻¹, 2209 reflections, 461 unobserved). Refinement by full-matrix least-squares was terminated at $R = 0.043$.

The propellanes¹ are compounds containing three rings that have one bond in common. There has been much speculation as to the molecular geometry of such systems when one or more of these rings is small (<5), particularly at the two carbon atoms that are common to all three rings.² The chemistry of "small ring propellanes," *i.e.*, those with less than 11 carbon atoms in the fused rings, has been reviewed by Ginsburg.³ Very interesting questions have been raised as to the hybridization of the bridgehead carbons.² The energy of a [2.2.2]propellane has been calculated as a function of the length of the central bond.⁴ The bridgehead carbon atoms might be expected to be coerced by geometry factors into a hybridization approximating sp², in which case the bridgehead bond would be formed by a σ overlap of the remaining p orbitals. This would suggest that the propellane bond should be longer and weaker than is normal for a carbon-carbon single bond. Indeed, Wiberg⁵ and Eaton² and their respective coworkers have found that the central bond in small ring propellanes is very reactive. For example, [3.2.2]- and [4.2.2]propellanes have been shown to add bromine readily at room temperature across the central single bond.² There are therefore good reasons for embarking on a detailed X-ray crystallographic study of a set of small ring propellanes with a view to measuring precise bond lengths and angles and to considering how these vary with ring size. We report now our results on the first of the set of [*n*. 2.2]propellanes ($n = 4, 3, 2$) that we have available and under investigation² (see structure I).



Experimental Section

Data measured are as follows: empirical formula, C₁₇H₁₉NO₄; mp 115.5–116.5°;³ space group $P2_1/n$ (no. 14); cell dimensions (least-squares refinement using reflections measured at $\pm\theta$) $a = 10.976$ (1), $b = 7.135$ (1), $c = 19.740$ (1) Å; $\beta = 90.43$ (1)°; $V = 1546$ Å³; $Z = 4$; $d_x = 1.294$ g/cc; $d_m = 1.28$ (1) g/cc (flotation in aqueous KI); radiation, Cu K α (graphite monochromator, λ 1.5418 Å); μ 4.69 cm⁻¹; crystal habit, monoclinic prismatic elongated along *b*; diffractometer, Nonius CAD4; crystal size for data collection, 0.125 \times 0.150 \times 0.570 mm. The intensity data were collected by a $\theta/2\theta$ scan with automatic scan and aperture expansion. A reflection was measured at the highest possible speed and then, if necessary, at a speed designed to achieve 2000 counts above background (a limit of 4 min was placed on measurement time). Reflections less than 20 counts above background (*ca.* 1 σ) in the preliminary scan were regarded as unobserved and not measured further. An attenuator was automatically inserted if the preliminary scan indicated a count rate greater than 50,000 counts/sec (the 1% linearity limit of the electronics). Three standard reflections, (028), (219), and (505), were measured sequentially at hourly intervals and also after every 51 reflections. The total drop in standard intensity was 3.5%, and two scale factors were assigned (approximately equal groups of reflections). For the purpose of structure determination and refinement, all reflections with $\theta < 50^\circ$ were included but only "observed" reflections ($> 3\sigma$) for $50^\circ < \theta \leq 65^\circ$ (1748 "observed" and 461 "unobserved" reflections). Lorentz and polarization corrections were applied by local programs, but no absorption corrections were made (azimuth scans indicated no significant intensity variation).

Structure Determination and Refinement

Quasi-normalized structure factor magnitudes (E values) were calculated by DATFIX program of the XRAY67 system⁶ (programs from this system were used for all calculations unless otherwise noted), and the structure was solved by symbolic addition as detailed by Silverton.⁷ The function minimized in least-squares refinement was $\Sigma[w(F_o - F_c)]^2$. Since the background, at the limit

Table I. Positional and Thermal Parameters for Heavier Atoms ($\times 10,000$)^a

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	3604 (2)	5121 (3)	9807 (1)	231 (3)	259 (6)	52 (1)	35 (3)	-21 (1)	12 (2)
O(2)	3632 (2)	2825 (3)	9113 (1)	263 (4)	400 (7)	36 (1)	-10 (4)	-10 (1)	-4 (2)
O(3)	3602 (2)	6653 (3)	1828 (1)	232 (3)	243 (5)	46 (1)	-72 (3)	-24 (1)	-3 (1)
O(4)	4158 (2)	9081 (2)	2471 (1)	143 (2)	226 (5)	35 (1)	-7 (2)	-16 (1)	-4 (1)
C(1)	3704 (2)	2129 (3)	253 (1)	87 (2)	232 (6)	34 (1)	15 (3)	-8 (1)	-6 (2)
C(2)	3995 (2)	2798 (3)	891 (1)	123 (3)	200 (6)	40 (1)	-4 (3)	-13 (1)	-13 (2)
C(3)	4044 (2)	1560 (4)	1420 (1)	128 (3)	236 (6)	33 (1)	-5 (4)	-15 (1)	-20 (2)
C(4)	3781 (2)	9669 (3)	1325 (1)	91 (2)	208 (6)	36 (1)	1 (3)	-10 (1)	-12 (2)
C(5)	3474 (2)	9054 (3)	681 (1)	131 (3)	204 (6)	40 (1)	0 (3)	-15 (1)	-17 (2)
C(6)	3450 (2)	254 (4)	138 (1)	125 (3)	258 (7)	34 (1)	11 (4)	-13 (1)	-23 (2)
C(7)	3830 (2)	8294 (4)	1895 (1)	111 (3)	235 (7)	37 (1)	-10 (4)	-9 (1)	-11 (2)
C(8)	4246 (2)	7885 (3)	3071 (1)	108 (3)	238 (6)	34 (1)	-17 (3)	-1 (1)	-5 (2)
C(9)	4225 (2)	9188 (4)	3681 (1)	120 (3)	291 (7)	41 (1)	19 (4)	5 (1)	-26 (2)
C(10)	4428 (3)	8082 (4)	4331 (1)	139 (3)	359 (8)	31 (1)	-6 (4)	13 (1)	-31 (2)
C(11)	5752 (2)	7407 (4)	4378 (1)	126 (3)	332 (8)	27 (1)	-5 (4)	4 (1)	-14 (2)
C(12)	6069 (2)	6293 (3)	3756 (1)	109 (3)	240 (6)	26 (1)	-14 (3)	2 (1)	-4 (2)
C(13)	5384 (2)	6702 (3)	3065 (1)	109 (3)	214 (6)	27 (1)	-15 (3)	3 (1)	-8 (2)
C(14)	6563 (3)	7494 (4)	2779 (1)	131 (3)	343 (8)	32 (1)	-10 (4)	16 (1)	5 (2)
C(15)	7273 (2)	6761 (4)	3395 (1)	107 (3)	337 (8)	35 (1)	4 (4)	4 (1)	-11 (2)
C(16)	5706 (3)	4217 (4)	3709 (1)	166 (4)	235 (7)	44 (1)	2 (4)	-8 (1)	3 (2)
C(17)	5230 (3)	4543 (4)	2981 (1)	161 (4)	229 (7)	39 (1)	-6 (4)	-8 (1)	-22 (2)
N	3639 (2)	3454 (4)	9682 (1)	122 (3)	294 (7)	38 (1)	11 (3)	-14 (1)	-1 (2)

^a The anisotropic temperature factor used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}hl + \beta_{31}kl)]$. Esd's in parentheses.

Table II. Positional Parameters for Hydrogen Atoms ($\times 1000$)^a

Atom	x/a	y/b	z/c	B
H(2)	420 (5)	404 (7)	94 (2)	6
(3)	425 (5)	194 (7)	183 (2)	6
(5)	338 (5)	787 (8)	65 (3)	6
(6)	319 (5)	986 (7)	-34 (2)	6
(8)	346 (4)	713 (6)	308 (2)	6
(9)	346 (4)	961 (6)	369 (2)	7
(18)	501 (4)	10 (6)	362 (2)	7
(10)	380 (4)	688 (6)	430 (2)	7
(20)	435 (4)	881 (6)	473 (2)	7
(11)	632 (4)	868 (6)	439 (2)	7
(22)	597 (4)	664 (6)	483 (2)	7
(14)	664 (4)	880 (7)	277 (2)	7
(28)	682 (4)	703 (6)	238 (2)	7
(15)	774 (4)	768 (6)	364 (2)	7
(30)	772 (4)	571 (6)	334 (2)	7
(16)	639 (4)	327 (6)	375 (2)	6
(32)	478 (4)	409 (6)	397 (2)	6
(17)	436 (4)	406 (6)	284 (2)	7
(34)	572 (4)	412 (6)	259 (2)	7

^a The temperature factors were assigned at approximately 1 unit higher than the attached carbon atoms (esd's in parentheses).

of the scan, was counted for one-half of the scan time, the weights used, following Peterson and Levy,⁸ were $w = 2F_o / [(LpSA)(I_s + 4(I_A + I_B) + 0.0004I_s^2)^{1/2}]$, where F_o is the scaled corrected structure factor, Lp is the Lorentz-polarization factor, S is the scale factor, A is the attenuation factor, I_s is the scan count, and I_A and I_B are the two background counts. Scattering factors for C, N, and O were taken from the "International Tables for X-ray Crystallography"⁹ and for H from Stewart, *et al.*¹⁰ The structure was refined by full-matrix least-squares using isotropic thermal parameters to an R factor of 0.14 and with anisotropic thermal parameters to $R = 0.09$. At this point, all the hydrogen atoms could be seen in a difference map with peak values between 0.35 and 0.55 e/Å,³ the noise level being less than 0.2 e/Å.³ Partition of the molecule into the propellane and benzoate portions was followed by refinement to convergence at a final R factor (based on observed reflections) of 0.043 (see note at end of paper concerning Supplementary Material). The final atomic parameters are given in Tables I and II.

Molecular Geometry

The bond lengths and angles for the title compound are given in Tables III and IV. An ORTEP¹¹ drawing of the

Table III. Interatomic Angles^a

Central atom	Other atoms	Angle	Central atom	Other atoms	Angle	
C ₁	N	C ₂	119.0	C ₁₁	C ₁₀	109.9
C ₁	N	C ₆	119.1	C ₁₂	C ₁₁	119.7
C ₁	C ₂	C ₆	121.9	C ₁₂	C ₁₁	117.8
C ₂	C ₁	C ₃	118.7	C ₁₂	C ₁₁	119.8
C ₃	C ₂	C ₄	121.0	C ₁₂	C ₁₂	88.1
C ₄	C ₃	C ₅	118.7	C ₁₂	C ₁₃	90.3
C ₄	C ₃	C ₇	121.9	C ₁₂	C ₁₅	113.8
C ₄	C ₅	C ₇	119.4	C ₁₃	C ₈	119.1
C ₅	C ₄	C ₆	121.5	C ₁₃	C ₈	120.0
C ₆	C ₁	C ₅	118.2	C ₁₃	C ₈	117.8
C ₇	C ₄	O ₃	123.4	C ₁₃	C ₁₂	89.4
C ₇	C ₄	O ₄	112.3	C ₁₃	C ₁₂	87.7
C ₇	O ₃	O ₄	124.4	C ₁₃	C ₁₄	114.7
C ₈	C ₉	O ₄	106.5	C ₁₃	C ₁₃	90.4
C ₈	C ₉	C ₁₃	111.5	C ₁₃	C ₁₂	90.4
C ₈	C ₁₃	O ₄	111.7	C ₁₆	C ₁₂	89.8
C ₉	C ₈	C ₁₀	110.3	C ₁₇	C ₁₃	90.8
C ₁₀	C ₉	C ₁₁	110.4			

^a Measured in degrees; all estimated standard deviations $\leq 0.2^\circ$.

Table IV. Bond Lengths^a

C(1)-C(2)	1.382 (4)	C(9)-C(10)	1.521 (4)
C(1)-C(6)	1.385 (4)	C(10)-C(11)	1.533 (4)
C(1)-N	1.472 (3)	C(11)-C(12)	1.507 (3)
C(2)-C(3)	1.369 (4)	C(12)-C(13)	1.578 (3)
C(3)-C(4)	1.392 (4)	C(12)-C(15)	1.543 (4)
C(4)-C(5)	1.383 (3)	C(12)-C(16)	1.536 (4)
C(4)-C(7)	1.494 (4)	C(13)-C(14)	1.525 (4)
C(5)-C(6)	1.372 (4)	C(13)-C(17)	1.559 (4)
C(7)-O(3)	1.205 (3)	C(14)-C(15)	1.533 (4)
C(7)-O(4)	1.317 (3)	C(16)-C(17)	1.543 (4)
C(8)-C(9)	1.521 (4)	N-O(1)	1.209 (3)
C(8)-C(13)	1.508 (3)	N-O(2)	1.215 (3)
C(8)-O(4)	1.462 (3)		

^a Estimated standard deviations in parentheses referring to last figure quoted.

molecule is given in Figure 1. In general, there are no surprising features as far as hydrogen atoms are concerned. The average C-H distance is 0.99 Å with an average esd of 0.05 Å. Average C-C-H angles are 120, 109.5, and 113° in the benzene, cyclohexane, and cyclobutane rings, respec-

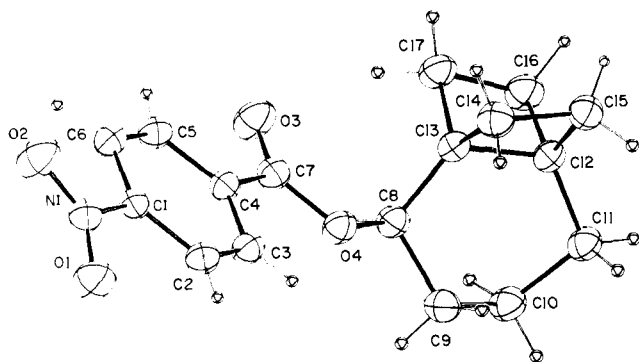


Figure 1. Molecular conformation and atomic numbering of the *p*-nitrobenzoate of 2-hydroxy[4.2.2]propellane. The ellipsoids represent 0.40 probability except for hydrogen atoms.

tively. With an average esd of 3° , individual variations from the mean are not significant except at C_{17} where there is some evidence of overcrowding. The bond lengths and angles of the *p*-nitrobenzoate moiety are well within the range of established values, although the benzene ring is not rigorously planar. (The χ^2 test indicates nonplanarity at better than the 0.01 level, but deviations are relatively small, *ca.* 3σ .) The nitrogen atom is 0.028 \AA below the least-squares plane of the benzene ring. The plane of the nitro group makes an angle of 15.6° with the plane of the aromatic ring. The carbon atom of the carboxyl group, C_7 , is 0.020 \AA above the plane containing C_1 , C_2 , C_3 , and C_4 , and this plane is 1.77° from the C_7 - O_3 - O_4 plane.

The more interesting part of the molecule is of course the propellane unit. As can be seen from Figure 1 and perhaps more clearly in Figure 2, the benzyloxy group has a quasi-equatorial configuration on the six-membered ring which itself assumes a somewhat flattened chair conformation. There is approximately a twofold axis along the line connecting the centers of the bridgehead and C_9 - C_{10} bonds. Deviations from an exact twofold axis relationship are less than 0.03 \AA . The least-squares planes of the cyclobutane rings make slightly different angles with the cyclohexane least-squares plane (56.4 and 57.9°). The angle between the mean planes of the cyclobutane rings is 66.6° . In the two cyclobutane rings, within the limits of accuracy, the atoms are symmetrically disposed with respect to the least-squares planes. In the $C_{12}C_{13}C_{14}C_{15}$ plane, all atoms are 0.068 \AA from the mean plane, and in the $C_{12}C_{13}C_{16}C_{17}$ plane, the distance is 0.061 \AA . Cyclobutane rings usually fall into two classes, puckered and flat, and in puckered rings the corresponding distance is usually 0.2 - 0.25 \AA ; however, in the present instance, the average nonbridgehead bond length (1.540 \AA) is somewhat shorter than that quoted for flat rings (1.562 \AA) or for puckered rings (1.555 \AA).¹² The slight puckering of the three rings of the propellane prevents complete eclipsing in each of the three pairs of carbons attached to the bridgeheads, C_{12} and C_{13} . Viewed along the C_{12} - C_{13} bond, as in Figure 2, the system has a "sense" in that the rear carbons, C_8 , C_{17} , and C_{14} , are advanced in a clockwise direction from the nearer atoms C_{11} , C_{15} , and C_{16} . This then is a "propeller" with blades pitched at 5.7 , 10.0 , and 9.1° , respectively.

Direct comparison with similar propellane structures is not possible since previously reported structures include an iron carbonyl derivative of an unsaturated propellane¹³ and a [4.4.3-aza] nucleus in 12-methyl-11,13-dioxo-12-azapentacyclo[4.4.3.0^{1,6}.0^{2,10}.0^{5,7}]tridecane-3,8-diene,¹⁴ both of which have severe perturbing influences (the second is not a "small ring propellane" by Ginsburg's³ definition). There is also a propellane moiety in the alkaloid annotin-

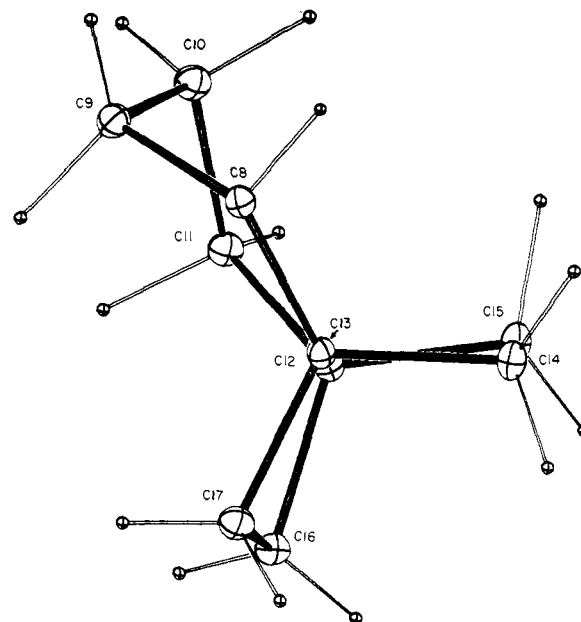


Figure 2. The [4.2.2]propellane viewed approximately along the axis of the "propeller."

ine¹⁵ [4-aza.4.2]. The most direct comparison is with the dichloro[3.2.1]propellane of Wiberg, Burgmaier, Shen, LaPlaca, Hamilton, and Newton.¹⁶ Although estimated standard deviations in the [3.2.1] compound are relatively large and only one ring is identical with those in the present study, there are similarities to the present study in that significantly short bridge-bridgehead bonds are reported in two of the rings. We intend to discuss the relationships further when a nearly completed study of a [3.2.2]propellane is submitted.

Electronic Structure

Three observations on the crystal structure are important in considering the electronic structure of [4.2.2]propellane. (a) The bridgehead carbon atom, C_{12} , is 0.26 \AA out of the plane of C_{11} , C_{15} , and C_{16} , and the corresponding value for C_{13} is 0.24 \AA . These distances, resulting from a motion of the bridgehead atoms toward the planes of their nonbridgehead substituents, represent substantial distortions from regular tetrahedral geometry where the distance would be 0.51 \AA . (b) The bridgehead-bridgehead bond length is 1.578 \AA which is considerably longer than the usual sp^3 - sp^3 length, although not greatly different from that found in strained cyclobutane rings, *e.g.*, cubane.¹⁷ (c) The two bonds of the six-membered ring attached to the bridgehead atoms are shorter than normal: C_8 - $C_{13} = 1.508 \text{ \AA}$, and C_{11} - $C_{12} = 1.507 \text{ \AA}$. (The length is comparable with that of a sp^2 - sp^3 bond.) The three observations are consistent with an approach toward sp^2 geometry at the bridgehead and with a consequent greater admixture of *p* character in the bridgehead-bridgehead bond.

The above electronic description is essentially confirmed by an INDO¹⁸ calculation on an unsubstituted hydrocarbon derived from the present structural results. A localization calculation¹⁹ following the method of Edmiston and Reudenberg²⁰ proved to be very slowly convergent. Because of the formidable computational expense, the calculation was terminated before total convergence was reached, but the numerical results indicate that localization was essentially complete.²¹

The bridgehead-bridgehead bond has enhanced *p*-character (sp^5) and a "total overlap population" ²² of 0.576 in-

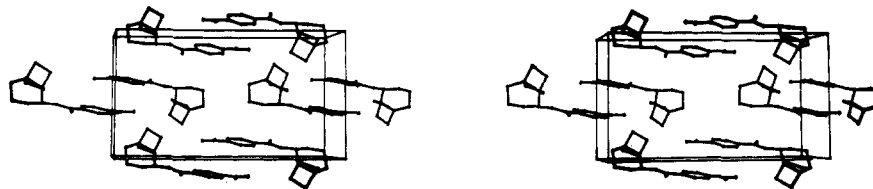


Figure 3. Packing diagram. The projection is approximately along *b*.

dicating a substantially weaker than normal bond (unstrained single bonds in organic compounds have total overlap populations of 0.7 to 0.8 as do the C-H bonds in this propellane). The approach to sp^2 hybridization is confirmed, but its use is confined to the bonds to the six-membered ring, the hybrids used in forming the bonds to the four-membered rings being essentially sp^3 . It is interesting and perhaps a little unexpected to find that the other hybrid involved in bonds to the six-membered ring is also sp^2 , but the short bond length is certainly consistent with the theoretical result. Other deviations from sp^3 hybridization in the six-membered ring are probably not very significant, and total overlap populations are indicative of normal strength bonds. The total overlap populations in the cyclobutane rings are not unexpected (0.670), and the only point of significance is the apparent asymmetry in the hybrids used by the external atoms, $sp^{2.6}$ to the bridgehead and $sp^{4.3}$ otherwise.

Molecular Packing

A stereoscopic diagram to show the packing is given as Figure 3. The closest intermolecular approaches (across the center of symmetry), $O_1-C_2 = 3.333 \text{ \AA}$, and $C_6-C_6 = 3.470 \text{ \AA}$, are not excessively short, and the packing appears reasonably efficient.

The conformation of the molecule is such that there is a close contact between O_3 and C_{17} (3.253 \AA), and there appears to be some slight consequent distortion of the molecule; $C_{13}-C_{17}$ is a little longer than other corresponding bonds, and the angle $C_{16}-C_{13}-C_{17}$ is a little larger than $C_{15}-C_{12}-C_{16}$.

Supplementary Material Available. A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material

from this paper only or microfiche ($105 \times 148 \text{ mm}$, 24X 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 \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7429.

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