

Geometry of Norbornane. X-Ray Crystal Structure of *exo-N*-(2-Norbornyl)benzamide

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Abstract. The crystal structure of the title compound was determined by direct methods. The crystal was found to be orthorhombic, with space group *Pbca*, and cell dimensions $a = 11.774$ (4), $b = 10.151$ (7), $c = 20.00$ (3). The structure was refined by full matrix least squares to $R = 0.057$. Several bonds which would be equivalent in the parent structure are definitely non-equivalent in this derivative. Using averaged values and combining them with literature data, the best composite structure for the parent hydrocarbon was deduced.

Although the norbornane ring system has been important in the field of organic chemistry for many years for a variety of reasons, the structural parameters of the parent compound are not very accurately known. Derivatives of norbornane have previously been studied by crystallographic methods, and the parent hydrocarbon has been studied by electron diffraction. Altona and Sundaralingam reviewed the crystallographic data that were available in 1972 and carried out a crystallographic study on the tosylate of 2-norbornanol¹ which uncovered an interesting case of crystal disorder but provided little structural information on the norbornyl system. They concluded only that bonds which correspond to the C₁-C₂ position in the parent hydrocarbon have lengths of 1.538 ± 0.003 Å.

More information is available from electron diffraction studies on the parent hydrocarbon in the gas phase and has been summarized by Kuchitsu.² The full structure was determined from these studies, but the probable errors in the bond lengths and angles are quite large (see Table V).

Because of the general importance of the norbornane ring system and the key place that this structure occupies in molecular mechanics calculations, a more accurate determination of the geometry is desirable. In particular, is the C₁-C₇ bond really significantly longer than ordinary C-C bonds? From the extremes of the probable error limits quoted, this bond could be as short as 1.536 Å (which is quite normal) or as long as 1.584 Å (an exceptionally long bond indeed). The bond angle at the bridgehead is also of interest for which reported values range from 92.8 to 96° as well as the angle θ (between the planes of the six-membered ring C₁-C₂-C₃-C₄ and C₄-C₅-C₆-C₁), reported values ranging from 109 to 114.8°.

Results

Since it does not seem possible to obtain increased accuracy by electron diffraction methods, and the molecule is too big to be conveniently studied by microwave techniques, use of the crystallographic method was clearly indicated. Because the molecule is nearly spherical, disordered crystals might be expected and have been found in various derivatives. To avoid disorder, a crystalline derivative which is reasonably high melting and which has an opportunity for hydrogen bonding is preferred. The benzoyl derivative of 2-norbornylamine [*exo-N*-(2-norbornyl)benzamide] appeared to be a good candidate and crystals were prepared without difficulty.

In order to achieve the desired state of refinement of the crystallographic structure, it was necessary to obtain data from three different crystals. Using data collected with Mo K α radiation, the structure was solved for the first crystal, but did not refine to our satisfaction ($R = 0.078$). Data from a second crystal using Mo K α and graphite monochromator refined to only $R = 0.084$. Data for the third crystal were collected using Cu K α radiation and included significantly more observed reflections which refined to $R = 0.057$. The structural results

reported in this paper are those obtained from the third crystal. Results from the first and second crystals are not substantially different, but are less precise than those from the third crystal. A summary of the crystallographic data is recorded in Table I. Positional coordinates and temperature factors, bond lengths, and bond angles are reported in Tables II, III, and IV, respectively. The numbering scheme used is shown in Figure 1.

Although the original purpose of the work was primarily to determine accurate bond lengths and angles for the parent norbornane, this system is evidently distorted by the substituent group, by crystal packing forces, or by both. In particular, the C₁-C₂ and C₃-C₄ bonds of 1.498 (5) and 1.518 (6) Å are significantly shorter than the corresponding C₁-C₆ and C₄-C₅ bonds of 1.571 (5) and 1.555 (7) Å. The average value of these four bonds, 1.536 (6) Å, compares favorably with the C₁-C₂ bond lengths reported by both Kuchitsu (1.539 ± 0.021 Å as determined by electron diffraction) and Altona and Sundaralingam (1.538 ± 0.003 by x-ray crystallography). The values for the C₂-C₃ and C₅-C₆ bonds, 1.555 (6) and 1.534 (7) Å, give an average value of 1.544 (7) Å, somewhat shorter than the electron diffraction C₂-C₃ value of 1.557 ± 0.025 . The average of the C₁-C₇ and C₄-C₇ bonds of 1.536 (6) Å also is shorter than the value determined by electron diffraction of 1.560 ± 0.024 Å. The overall average of C-C bond lengths from the x-ray data is 1.538 (6) Å compared to Kuchitsu's value of 1.548 ± 0.003 Å. Table V shows a comparison of the data from this study and the values determined by electron diffraction studies of the parent norbornane. The apparent distortion of the system by the benzamide substituent is under further study.

As expected, the C-C-C bond angles of the norbornyl segment are all less than the tetrahedral angle, indicating strain within the system. Particularly, the C₁-C₇-C₄ bridge angle is only 94.3 (3)°, which is in reasonable agreement with the electron diffraction results of 93.1 ± 1.7 °.

The segment of the molecule containing C₁, C₂, C₃, and C₄ is essentially planar with average deviations from the plane of

Table I. Summary of Crystallographic Data

Molecular formula	C ₁₄ H ₁₇ NO
Molecular weight	215.3 g/mol
Linear absorption coefficient	5.950 cm ⁻¹ (Cu K α)
Calculated density	1.20 g/cm ³
Crystal dimensions (crystal no. 3)	0.5 × 0.2 × 0.1 mm
Space group	<i>Pbca</i>
Cell dimensions	$a = 11.774$ (4), $b = 10.151$ (7), $c = 20.00$ (3)
	$Z = 8$, $V = 2390$ Å ³

Table II. Positional Coordinates^a and Temperature Factors^b for *exo-N*-(2-Norbornyl)benzamide

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C ₁	0.290 73 (32)	0.157 98 (33)	0.528 98 (20)	0.005 76 (28)	0.005 57 (34)	0.003 20 (12)	0.000 51 (54)	-0.000 67 (32)	0.000 22 (35)
C ₂	0.359 96 (32)	0.160 93 (34)	0.466 30 (18)	0.006 79 (30)	0.005 73 (35)	0.002 64 (11)	-0.000 72 (56)	-0.000 96 (34)	-0.001 24 (34)
C ₃	0.447 96 (35)	0.272 60 (47)	0.479 41 (23)	0.005 64 (31)	0.013 08 (54)	0.003 32 (14)	-0.006 26 (75)	-0.000 31 (36)	-0.002 28 (48)
C ₄	0.418 67 (42)	0.318 53 (38)	0.549 39 (22)	0.012 06 (49)	0.006 42 (39)	0.003 39 (14)	-0.005 59 (72)	-0.004 19 (43)	-0.002 49 (41)
C ₅	0.452 86 (51)	0.208 71 (45)	0.599 76 (27)	0.013 03 (55)	0.009 93 (51)	0.003 80 (17)	-0.006 04 (90)	-0.007 32 (53)	0.001 25 (49)
C ₆	0.368 67 (40)	0.096 97 (38)	0.584 62 (22)	0.009 22 (40)	0.007 52 (42)	0.003 20 (14)	0.000 37 (68)	-0.003 50 (41)	0.000 12 (39)
C ₇	0.288 22 (42)	0.303 68 (35)	0.549 12 (23)	0.011 96 (51)	0.005 79 (40)	0.003 12 (14)	0.006 94 (68)	0.003 65 (44)	0.000 21 (38)
C ₈	0.240 27 (30)	0.090 35 (29)	0.372 82 (16)	0.005 84 (29)	0.004 49 (30)	0.002 06 (9)	0.000 00 (52)	-0.000 55 (29)	-0.000 83 (28)
C ₉	0.175 77 (28)	0.125 76 (30)	0.311 96 (15)	0.005 78 (28)	0.004 82 (30)	0.001 58 (8)	0.001 18 (48)	-0.000 32 (26)	-0.000 43 (27)
C ₁₀	0.197 93 (33)	0.239 28 (38)	0.275 57 (19)	0.007 18 (30)	0.007 54 (39)	0.002 13 (10)	-0.000 19 (62)	0.000 22 (32)	0.000 44 (34)
C ₁₁	0.133 96 (38)	0.267 28 (45)	0.218 81 (19)	0.010 15 (40)	0.010 69 (49)	0.002 14 (11)	0.003 08 (80)	0.001 23 (38)	0.002 10 (40)
C ₁₂	0.048 73 (40)	0.183 62 (47)	0.198 65 (20)	0.009 61 (42)	0.014 13 (57)	0.002 04 (11)	0.005 06 (86)	-0.001 55 (38)	-0.001 63 (44)
C ₁₃	0.026 80 (37)	0.070 07 (43)	0.234 44 (20)	0.008 35 (42)	0.011 14 (49)	0.002 76 (14)	0.001 23 (73)	-0.002 52 (40)	-0.002 17 (41)
C ₁₄	0.090 50 (32)	0.041 30 (36)	0.290 26 (19)	0.006 80 (32)	0.007 03 (38)	0.002 38 (11)	-0.000 62 (59)	-0.000 97 (33)	-0.001 37 (36)
O	0.247 96 (25)	-0.026 58 (20)	0.391 42 (12)	0.011 93 (26)	0.003 12 (20)	0.003 14 (8)	-0.000 84 (43)	-0.003 78 (26)	0.000 36 (22)
N	0.290 62 (27)	0.187 95 (28)	0.407 18 (15)	0.007 68 (27)	0.003 82 (28)	0.002 27 (8)	-0.000 86 (44)	-0.002 66 (25)	-0.000 86 (26)
HC ₁	0.2042 (33)	0.1096 (37)	0.5233 (18)	2.2 (8)					
HC ₂	0.4049 (36)	0.0687 (43)	0.4604 (20)	4.0 (10)					
H ₁ C ₃	0.5305 (40)	0.2371 (46)	0.4748 (22)	4.6 (12)					
H ₂ C ₃	0.4351 (39)	0.3546 (44)	0.4441 (22)	4.4 (12)					
HC ₄	0.4516 (41)	0.4039 (48)	0.5606 (24)	5.4 (13)					
H ₁ C ₅	0.5327 (49)	0.1709 (53)	0.5880 (27)	6.9 (17)					
H ₂ C ₅	0.4444 (37)	0.2401 (46)	0.6493 (24)	4.2 (12)					
H ₁ C ₆	0.3139 (42)	0.0754 (47)	0.6360 (24)	5.7 (13)					
H ₂ C ₆	0.4163 (36)	0.0135 (46)	0.5662 (21)	4.6 (12)					
H ₁ C ₇	0.2531 (38)	0.3219 (40)	0.5982 (22)	4.0 (10)					
H ₂ C ₇	0.2471 (34)	0.3576 (39)	0.5135 (19)	2.5 (9)					
HC ₁₀	0.2572 (34)	0.2950 (38)	0.2910 (18)	2.3 (9)					
HC ₁₁	0.1570 (36)	0.3488 (42)	0.1930 (21)	3.7 (11)					
HC ₁₂	0.0014 (34)	0.2005 (39)	0.1544 (21)	3.2 (10)					
HC ₁₃	-0.0431 (42)	0.0096 (51)	0.2183 (22)	5.4 (13)					
HC ₁₄	0.0742 (33)	-0.0290 (40)	0.3192 (19)	2.7 (10)					
HN	0.2780 (38)	0.2618 (48)	0.3942 (22)	4.0 (12)					

^a Figures in parentheses are estimated standard deviations with respect to the last digit quoted. ^b Anisotropic temperature factors have the form $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

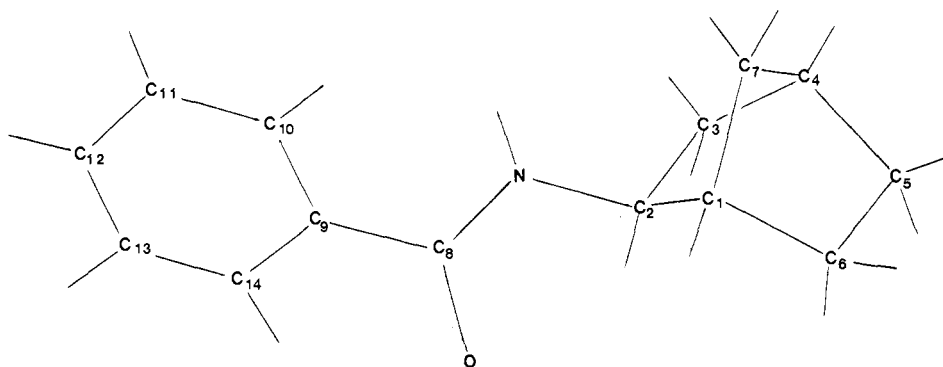


Figure 1. Numbering scheme used in the x-ray analysis. The numbering of the norbornyl portion corresponds to the standard numbering applied to bicyclic systems.

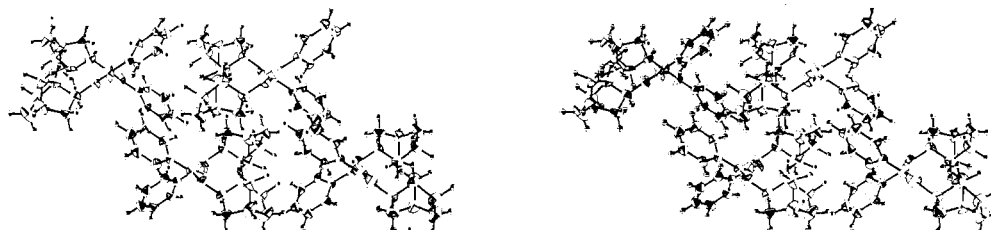


Figure 2. ORTEP stereoscopic unit cell packing diagram. Axis *a* is vertical and axis *c* is horizontal. The amide hydrogen bonding runs parallel to the *b* axis. Thermal ellipsoids are drawn at 50% probability level; for clarity, H atoms are drawn isotropically at 50% probability level with *B* = 1.0.

Table III. Distances between Bonded Atoms

Atoms	Distance, Å ^a	Atoms	Distance, Å ^a
C ₁ -C ₂	1.498 (5)	C ₁ -HC ₁	1.14 (4)
C ₁ -C ₆	1.571 (5)	C ₂ -HC ₂	1.08 (4)
C ₁ -C ₇	1.529 (5)	C ₃ -H ₁ C ₃	1.04 (5)
C ₂ -C ₃	1.555 (6)	C ₃ -H ₂ C ₃	1.10 (4)
C ₃ -C ₄	1.518 (6)	C ₄ -HC ₄	0.97 (5)
C ₄ -C ₅	1.555 (7)	C ₅ -H ₁ C ₅	1.04 (6)
C ₄ -C ₇	1.543 (7)	C ₅ -H ₂ C ₅	1.05 (5)
C ₅ -C ₆	1.534 (7)	C ₆ -H ₁ C ₆	1.23 (5)
N-C ₂	1.465 (5)	C ₆ -H ₂ C ₆	1.08 (5)
N-C ₈	1.342 (4)	C ₇ -H ₁ C ₇	1.08 (4)
O-C ₈	1.244 (4)	C ₇ -H ₂ C ₇	1.02 (4)
C ₈ -C ₉	1.481 (4)	N-HN	0.81 (5)
C ₉ -C ₁₀	1.386 (5)	C ₁₀ -HC ₁₀	0.95 (4)
C ₁₀ -C ₁₁	1.394 (6)	C ₁₁ -HC ₁₁	1.01 (4)
C ₁₁ -C ₁₂	1.374 (6)	C ₁₂ -HC ₁₂	1.06 (4)
C ₁₂ -C ₁₃	1.379 (6)	C ₁₃ -HC ₁₃	1.08 (5)
C ₁₃ -C ₁₄	1.378 (6)	C ₁₄ -HC ₁₄	0.94 (4)
C ₁₄ -C ₉	1.388 (5)		

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

only 0.004 Å. The opposite side of the system containing C₁, C₆, C₅, and C₄ is somewhat less planar with average deviations of 0.014 Å. The angle between these two planes, θ , is 112.1°, again in good agreement with electron diffraction results of 113.1 ± 1.8°. The plane containing C₁, C₇, and C₄ forms angles of 124.3 and 123.6° with the two planes described above. Table VII gives equations for the various planes in the molecule and deviations for each atom from the planes; Table VIII lists angles between these planes.

The amide portion of the molecule containing C₂, N, C₈, O, C₉, and HN is essentially planar with average deviations of 0.022 Å from the plane. The atoms of the benzene ring are also planar showing average deviations of 0.005 Å from the plane defined by C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, and C₁₄. These two planes are rotated from each other by 25.4° with dihedral

Table IV. Angles between Bonded Atoms

Atoms	Angle, deg (esd)	Atoms	Angle, deg (esd)
C ₂ -C ₁ -C ₆	106.6 (3)	C ₂ -C ₃ -H ₁ C ₃	111 (3)
C ₂ -C ₁ -C ₇	102.3 (3)	C ₂ -C ₃ -H ₂ C ₃	110 (2)
C ₆ -C ₁ -C ₇	101.7 (3)	C ₄ -C ₃ -H ₁ C ₃	114 (2)
N-C ₂ -C ₁	112.3 (3)	C ₄ -C ₃ -H ₂ C ₃	109 (2)
N-C ₂ -C ₃	111.8 (3)	H ₁ C ₃ -C ₃ -H ₂ C ₃	109 (3)
C ₁ -C ₂ -C ₃	103.6 (3)	C ₃ -C ₄ -HC ₄	113 (3)
C ₂ -C ₃ -C ₄	103.2 (3)	C ₅ -C ₄ -HC ₄	112 (3)
C ₃ -C ₄ -C ₅	108.8 (4)	C ₇ -C ₄ -HC ₄	119 (3)
C ₃ -C ₄ -C ₇	101.1 (4)	C ₁ -C ₆ -H ₁ C ₆	111 (2)
C ₅ -C ₄ -C ₇	101.0 (4)	C ₁ -C ₆ -H ₂ C ₆	112 (2)
C ₄ -C ₅ -C ₆	103.4 (4)	C ₅ -C ₆ -H ₁ C ₆	108 (2)
C ₁ -C ₆ -C ₅	103.2 (3)	C ₅ -C ₆ -H ₂ C ₆	108 (2)
C ₁ -C ₇ -C ₄	94.3 (3)	H ₁ C ₆ -C ₆ -H ₂ C ₆	115 (3)
C ₂ -N-C ₈	121.6 (3)	C ₁ -C ₇ -H ₁ C ₇	114 (2)
O-C ₈ -N	120.9 (3)	C ₁ -C ₇ -H ₂ C ₇	110 (2)
O-C ₈ -C ₉	121.0 (3)	C ₄ -C ₇ -H ₁ C ₇	111 (2)
N-C ₈ -C ₉	118.1 (3)	C ₄ -C ₇ -H ₂ C ₇	115 (2)
C ₈ -C ₉ -C ₁₀	122.5 (3)	H ₁ C ₇ -C ₇ -H ₂ C ₇	111 (3)
C ₈ -C ₉ -C ₁₄	118.7 (3)	C ₂ -N-HN	123 (3)
C ₁₀ -C ₉ -C ₁₄	118.8 (3)	C ₈ -N-HN	116 (3)
C ₉ -C ₁₀ -C ₁₁	119.8 (4)	C ₉ -C ₁₀ -HC ₁₀	117 (2)
C ₁₀ -C ₁₁ -C ₁₂	120.6 (4)	C ₁₁ -C ₁₀ -HC ₁₀	123 (2)
C ₁₁ -C ₁₂ -C ₁₃	119.8 (4)	C ₁₀ -C ₁₁ -HC ₁₁	116 (2)
C ₁₂ -C ₁₃ -C ₁₄	119.8 (4)	C ₁₂ -C ₁₁ -HC ₁₁	123 (2)
C ₉ -C ₁₄ -C ₁₃	121.2 (3)	C ₁₁ -C ₁₂ -HC ₁₂	122 (2)
C ₂ -C ₁ -HC ₁	114 (2)	C ₁₃ -C ₁₂ -HC ₁₂	118 (2)
C ₆ -C ₁ -HC ₁	115 (2)	C ₁₂ -C ₁₃ -HC ₁₃	117 (3)
C ₇ -C ₁ -HC ₁	115 (2)	C ₁₄ -C ₁₃ -HC ₁₃	123 (3)
N-C ₂ -HC ₂	110 (2)	C ₉ -C ₁₄ -HC ₁₄	115 (2)
C ₁ -C ₂ -HC ₂	110 (2)	C ₁₃ -C ₁₄ -HC ₁₄	124 (2)
C ₃ -C ₂ -HC ₂	109 (2)		

angles O-C₈-C₉-C₁₀ of -155.2 (3)° and O-C₈-C₉-C₁₄ of 24.3 (5)°. Table VI gives selected dihedral angles for the molecule.

A packing diagram is shown in Figure 2. The intermolecular hydrogen bonding between the hydrogen of the nitrogen and

Table V. Comparison of Various Measurements and Calculations of the Norbornane Structure

Parameters	Direct x ray	Average x ray	Electron diffraction ²	Electron diffraction ^{2,13}	Composite structure	Molecular mechanics	
(C-C) _{av}	1.538 (6)	1.538 ± 0.012	1.548 ± 0.003	1.545	1.544	1.541	
C ₁ -C ₂	C ₁ -C ₂	1.498 (5)	1.536 ± 0.018	1.539 ± 0.012	1.534 ± 0.014	1.536	1.542
	C ₃ -C ₄	1.518 (6)					
	C ₁ -C ₆	1.571 (5)					
	C ₄ -C ₅	1.555 (7)					
C ₂ -C ₃	C ₂ -C ₃	1.555 (6)	1.544 ± 0.021	1.557 ± 0.025	1.578 ± 0.018	1.561	1.541
	C ₅ -C ₆	1.534 (7)					
C ₁ -C ₇	C ₁ -C ₇	1.529 (5)	1.536 ± 0.018	1.560 ± 0.024	1.560 ± 0.024	1.544	1.538
	C ₄ -C ₇	1.543 (7)					
	C ₁ -C ₇ -C ₄	94.3 (3) ^o	94.3 ± 0.6	93.1 ± 1.7	95.3 ± 1.6	94.3	92.5
θ	112.1 ^o	112.1	113.1 ± 1.8	111.3	112.2	113.3	
(C-H) _{av}	1.076 (47)	1.076 ± 0.094	1.126 ± 0.005	1.11 ± 0.01	1.12		
H-C-H _{av}	112 ^o (4)	112 ± 8	110 ± 4	111 ± 4	111		

Table VI. Selected Dihedral Angles

Atoms	Angle, deg (esd) ^a	Atoms	Angle, deg (esd)
C ₁ -C ₂ -C ₃ -C ₄	-0.9 (4)	C ₂ -N-C ₈ -O	2.3 (5)
C ₄ -C ₅ -C ₆ -C ₁	2.6 (5)	C ₂ -N-C ₈ -C ₉	-177.4 (3)
C ₇ -C ₁ -C ₂ -C ₃	34.5 (4)	O-C ₈ -C ₉ -C ₁₀	-155.2 (3)
C ₇ -C ₁ -C ₆ -C ₅	-33.3 (4)	O-C ₈ -C ₉ -C ₁₄	24.3 (5)
C ₂ -C ₃ -C ₄ -C ₇	-35.5 (4)	N-C ₈ -C ₉ -C ₁₀	24.5 (5)
C ₇ -C ₄ -C ₅ -C ₆	37.3 (4)	N-C ₈ -C ₉ -C ₁₄	-156.0 (3)

^a The dihedral angle I-J-K-L is considered positive in sign if the vector K-L is clockwise from vector J-I when viewed down J-K and negative if counterclockwise.

the carbonyl oxygen occurs parallel to the *b* axis. The intermolecular N...O distance is 2.942 (3) Å with a distance of 2.16 (5) Å between the hydrogen and the oxygen. The only other intermolecular distance less than 3.5 Å between nonhydrogen atoms is 3.379 (4) Å between C₁₀ and O.

Discussion

Our principal objective in this work was to obtain a more accurate structure of the norbornane ring system. Because we are dealing with a substituted molecule in a condensed phase, there are several bond distances which would be identical in the parent unsubstituted molecule in the gas phase which have different values here. In order to use the present data to derive the structural quantities for the parent ring system, assumptions are necessary. It will be assumed that the bonds which would be equivalent in the absence of a substituent may have their lengths and angles averaged in order to obtain the corresponding hydrocarbon value. This is an assumption which cannot be completely justified, but it is noted that the values obtained by Altona and Sundaralingam, by Kuchitsu, and by ourselves all seem to be comparable on that basis.

In order to compare these results with the electron diffraction results, the probable errors in the derived distances must be estimated. We have taken three times the estimated standard deviations in the x-ray work as being equal to the probable error in cases where very nonequivalent quantities are being averaged, and two times the esd in other cases. These results are summarized in Table V.

The best composite structure was obtained by taking the averaged x-ray structure and the two electron diffraction structures, and averaging the three together, weighing each according to the inverse of the experimental error. From ex-

Table VII. Equations of Planes and Distances from Planes

Atom	<i>P</i>	<i>Q</i>	<i>R</i>	Distance, Å (esd)
Plane A	Equation: -0.6291 <i>P</i> + 0.6753 <i>Q</i> - 0.3849 <i>R</i> + 5.159 = 0.0			
C ₁	3.422	1.599	10.607	0.004 (5)
C ₂	4.237	1.629	9.350	-0.005 (5)
C ₃	5.272	2.760	9.613	0.005 (5)
C ₄	4.927	3.225	11.017	-0.004 (5)
Plane B	Equation: 0.6137 <i>P</i> - 0.3808 <i>Q</i> - 0.6917 <i>R</i> + 5.836 = 0.0			
C ₄	4.927	3.225	11.017	0.012 (13)
C ₅	5.330	2.113	12.027	-0.017 (13)
C ₆	4.339	0.982	11.723	0.016 (13)
C ₁	3.422	1.599	10.607	-0.011 (13)
Plane C	Equation: 0.8196 <i>P</i> - 0.0928 <i>Q</i> - 0.5653 <i>R</i> + 1.993 = 0			
C ₂	4.237	1.629	9.350	0.028 (26)
N	3.420	1.903	8.165	0.004 (26)
HN	3.272	2.650	7.904	-0.039 (26)
C ₈	2.828	0.915	7.476	0.000 (26)
O	2.918	-0.269	7.849	-0.027 (26)
C ₉	2.069	1.273	6.256	0.034 (26)
Plane D	Equation: 0.6591 <i>P</i> - 0.5013 <i>Q</i> - 0.5606 <i>R</i> + 2.781 = 0.0			
C ₈	2.828	0.915	7.476	-0.006 (6)
C ₉	2.069	1.273	6.256	-0.002 (6)
C ₁₀	2.329	2.422	5.526	0.003 (6)
C ₁₁	1.577	2.706	4.388	0.003 (6)
C ₁₂	0.574	1.859	3.983	-0.007 (6)
C ₁₃	0.315	0.709	4.701	-0.003 (6)
C ₁₄	1.065	0.418	5.820	0.010 (6)
Plane E	Equation: 0.0218 <i>P</i> - 0.2635 <i>Q</i> + 0.9644 <i>R</i> - 9.882 = 0.0			
C ₁	3.422	1.599	10.607	0.001 (9)
C ₇	3.392	3.074	11.011	0.001 (9)
C ₄	4.927	3.225	11.017	0.000 (9)
HC ₁	2.404	1.110	10.494	-0.001 (9)
HC ₄	5.315	4.089	11.242	-0.001 (9)

Table VIII. Angles between Planes

Planes	Angle, deg
A,B	112.1
A,E	124.2
B,E	123.6
C,D	25.4
A,C	111.1

amination of this composite structure, the following points are evident: (1) The overall bond length (1.544 Å) is about 0.01 Å longer than that found in cyclohexane (1.536 Å).³ (2) The C₁-C₂ bond length is unexceptional. (3) The C₂-C₃ bond

length is somewhat long, but not unexpectedly so, since it is an eclipsed conformation. (4) The C₁-C₇ bond length has a value which is only a little longer than that found in cyclohexane, and it is shorter than the C₂-C₃ bond length. This is an important point in force field calculations, and it contrasts with the quite long bond length found by Kuchitsu. The composite structure value is in reasonable agreement with all of the experimental values, however.

The crucial peak angle value found for the composite structure is 94.3°, while the angle between the planes which comprise the six-membered ring is 112.2°.

Comparisons of the molecular mechanics calculations obtained⁴ with our 1977 force field (MM2) with the composite structure are shown in Table V. These calculations were completed before the current experimental work. The calculations show the C₂-C₃ bond to be slightly too short, which yields a bridgehead angle which is also somewhat too small.

Experimental Section

exo-2-Norbornylamine (Aldrich Chemical) was redistilled, bp 142-144 °C (lit.⁵ 143-144 °C). It was converted to the amide with benzoyl chloride and aqueous sodium hydroxide and the product was twice recrystallized from acetone, mp 150-150.5 °C (lit.⁶ 149-150 °C). Crystals suitable for x-ray analysis were obtained from a mixture of dry methanol and ethanol.

The samples of *exo*-N-(2-norbornyl)benzamide mounted were cut from larger needle crystals. They were found to be in the orthorhombic space group *Pbc*a from systematic absences observed by means of an Enraf-Nonius CAD-4 automated diffractometer. The orientation matrix and cell dimensions were calculated using 15 accurately centered reflections with θ values ranging from 4.4 to 25.3°. A summary of the crystal data is provided in Table I.

Intensity data from the first crystal were collected to a maximum of $\theta = 30^\circ$, using an ω - 2θ scan technique and Mo K α radiation with a Zr filter. A total of 2430 reflections were measured, of which 918 were considered unique, nonzero diffraction maxima after rejecting all data below $2\sigma_1$. Control reflections monitored after each block of 100 reflections showed no significant decomposition of the crystal over the period of data collection. The data were corrected for Lorentz-polarization effects⁷ and reduced to an absolute scale by the method of Wilson utilizing the program FAME.⁸

The structure was solved from the first data set by direct methods using MULTAN.⁹ Using E 's ≥ 1.5 , MULTAN produced one set of phases with an ABSFOM = 2.83 that was significantly higher than the remaining phase sets. The E map¹⁰ from this phase set showed all 16 of the nonhydrogen atoms. Several cycles of isotropic least-square refinement¹¹ of these positions on the complete data set gave $R = 0.168$. Several more cycles of anisotropic refinement produced an R of 0.125. At this stage, difference maps were employed to locate the 17 hydrogen atoms. Final refinement, using isotropic temperature factors for the hydrogens and anisotropic temperature factors for all other atoms, gave $R = 0.078$. Difference maps after the final refinement showed no evidence of disorder in the structure.

Since the standard deviations in the bond lengths and angles were still somewhat large at this stage of refinement the data were recol-

lected using Mo K α radiation with a graphite monochromator instead of the Zr filter. Of the total of 2098 measured, only 631 could be considered observed after rejecting those below $2\sigma_1$. Following data reduction, refinement of the positions determined from the first crystal using the second data set gave an R of 0.085 and standard deviations still too large for the purposes of the investigation.

Intensity data were collected on a third crystal using Cu K α radiation and a graphite monochromator. Collecting to a maximum θ of 70°, 2269 reflections were measured. Of these, 1280 were used in the refinement as unique, nonzero diffraction maxima, rejecting those below $3\sigma_1$. Again no decomposition was observed in the control reflections monitored during data collection. The data were corrected for Lorentz and polarization factors. Using the positions determined from the first crystal, full-matrix least-squares refinement using weights of $1/\sigma_{F_o}^2$ gave a final R value of 0.057. The final positional and thermal parameters are listed in Table II.

Acknowledgments. The authors are grateful to Ms. Patricia Teaford for the synthesis studies directed at compounds used for this work. We are also grateful to the National Science Foundation for support of this work (Grant NSF 74-08071)

Supplementary Material Available: Table of h , $K = L = F_o$, and F_o for *exo*-N-(2-norbornyl)benzamide (9 pages). Ordering information is given on any current masthead page.

References and Notes

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- (8) The computer program FAME was written by R. A. Dewar, A. Stone, and E. B. Fleischer, The University of Chicago, Chicago, Ill.
- (9) The computer program MULTAN was written by P. Main and M. M. Woolfson, University of York, York, England, and G. Germain, Universite de Louvain, Louvain, Belgium.
- (10) The Fourier program used is FORDAP written by Z. Zalkin, Lawrence Radiation Laboratory, Livermore, Calif.
- (11) The full-matrix, least-squares program (UGALS) used in refinement was written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood and modified by M. G. Newton for the IBM-360.
- (12) The standard deviation of F_{hkl} , σ_{F_o} , is obtained from counting statistics and is computed by

$$\sigma_{F_o}^2 = \frac{1}{4Lp} \left[\frac{(at+1)l + 4(B_l + B_r) + (Kl)^2}{s\{l - 2(B_l + B_r)\}} \right]$$
 where l = total measured peak intensity and backgrounds, B_l = left background, B_r = right background, $l_i = \{(at+1)/s\}l - 2(B_l + B_r)$, 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 = 2.63, K = standard deviation for instrumental instability (the value of K is estimated from control reflections), Lp = Lorentz-polarization correction.
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