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Crystal and Molecular Structure of the *N,N*-Dimethylurea Derivatives of *exo*-5-Ethoxy-5-isocyanatobicyclo[2.1.0]-pentane and *exo*-6-Ethoxy-6-isocyanatobicyclo[3.1.0]hexane. Confirmation of the γ-Steric Shift in Nitrogen-15 Nuclear Magnetic Resonance as a Tool for Stereochemical Assignment[1]

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Abstract: The single-crystal X-ray analyses of the *N,N*-dimethylurea derivatives of *exo*-5-ethoxy-5-isocyanatobicyclo[2.1.0]-pentane (**8**) and *exo*-6-ethoxy-6-isocyanatobicyclo[3.1.0]hexane (**5**) are described. The analyses were performed to establish the stereochemistry of **5** and **8** and to prove that the γ-steric shift in ^{15}N NMR spectroscopy can be used to assign the stereochemistry of a nitrogen substituent relative to a carbon substituent in a rigid system. The bicyclohexane **5** crystallizes in the space group $P2_1/n$ with four molecules per unit cell of dimensions a = 8.053 (2), b = 17.251 (7), and c = 9.123 (2) Å, and β = 107.11 (2)°. From 1690 unique, observed reflections collected on an automated four-circle diffractometer, the structure was solved and refined to final values for the discrepancy indices of R = 0.049 and R_2 = 0.061. The bicyclopentane **8** crystallizes in the space group *Pbca* with eight molecules per unit cell of dimensions a = 10.187 (5), b = 13.822 (7), and c = 16.207 (7) Å. From 900 unique, observed reflections similarly collected, the structure was solved and refined to final values for the discrepancy indices of R = 0.044 and R_w = 0.057. The molecular structure data are compared with data in the literature for other bicyclo[2.1.0]pentanes and bicyclo[3.1.0]hexanes. This comparison indicates that there is some error in a recent structure determination of bicyclo[3.1.0]hexane by a combination of microwave spectroscopy and electron diffraction. ^{15}N NMR chemical shifts for the secondary urea nitrogens of **5** and **8** are discussed in terms of intramolecular contacts. The chemical shifts are consistent with a downfield, sterically induced δ shift and a dominant, upfield, sterically induced γ shift.

The γ-steric shift in ^{13}C NMR has been used extensively for organic structural analysis[2] including conformational analysis,[3] configurational assignments,[4] and analysis of the spectra of complex molecules.[5] We have recently proposed without absolute proof that an analogous γ-steric shift in ^{15}N NMR can be used to assign the stereochemical relationship of a nitrogen substituent to a γ-carbon substituent in a rigid system.[6] Here we report X-ray crystallographic data which unambiguously substantiate our previous stereochemical assignments and which confirm the γ-steric shift in ^{15}N NMR as a tool for stereochemical assignment.

Prior evidence that the γ shift in ^{15}N NMR is a sterically induced upfield shift comes from the work of Roberts and coworkers.[7] They have shown that linear regression analysis of the ^{15}N chemical shifts of acyclic amines in terms of α, β, γ, δ, and ε substituent effects gives a γ effect of +2.7 ppm. Comparison of the ^{15}N resonances of isobutylamine and (cyclopropylmethyl)amine suggests the steric nature of the γ effect. The ^{15}N absorption of (cyclopropylmethyl)amine appears 4.6 ppm downfield from the ^{15}N absorption of isobutylamine, presumably because the γ carbons sterically interact less with the nitrogen in (cyclopropylmethyl)amine. A dominant γ-steric effect is also given as the simplest interpretation for the observation that the nitrogens of *cis*-1,2-diaminocyclobutane

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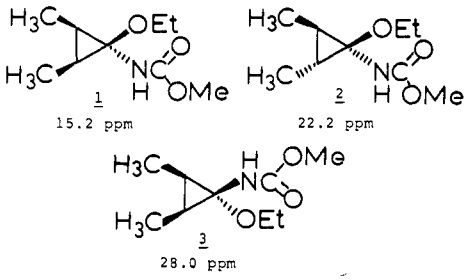
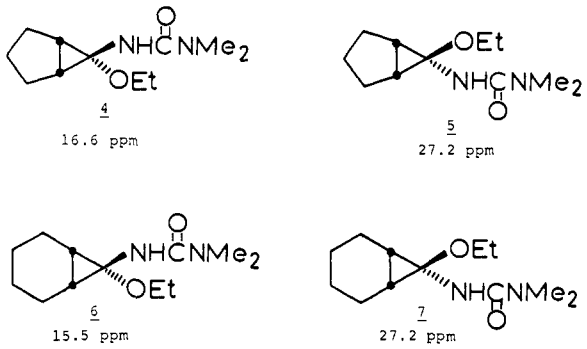
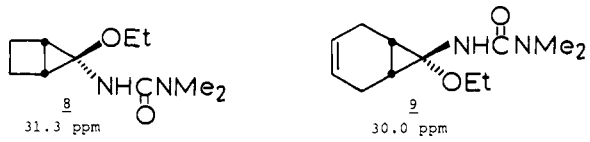
absorb at 13.5 ppm higher field than the nitrogens of *trans*-1,2-diaminocyclobutane; however, stereoelectronic and hydrogen bonding effects are also thought to be important.[7] A γ-steric shift is given as the simplest interpretation for the chemical shift separation of the ^{15}N resonances of the α and β anomers of 2-amino-2-deoxy-D-mannose and 2-acetamido-2-deoxy-D-mannose.[8] Recently Roberts and co-workers[9] have demonstrated that there is a linear correlation between natural abundance ^{15}N NMR chemical shifts of piperidines and decahydroquinolines and ^{13}C NMR chemical shifts of their hydrocarbon analogues. In particular, a gauche γ-methyl or methylene group results in an upfield shift which appears to be sterically induced.

We have observed[6] that the ^{15}N resonances of the methyl carbamates **1** and **3** of the diastereoisomeric *cis*-2,3-dimethylethoxycyclopropyl isocyanates differ by 12.8 ppm and that the ^{15}N resonance of the methyl carbamate **2** of *trans*-2,3-dimethylethoxycyclopropyl isocyanate appears at an intermediate position upfield from the internal standard, 2-pyrrolidone. Further, the ^{15}N resonances of the secondary nitrogens of the diastereoisomeric dimethylurea derivatives **4** and **5** of the 6-ethoxy-6-isocyanatobicyclo[3.1.0]hexanes differ by 10.6 ppm. Recently we have determined that the ^{15}N resonances of the secondary nitrogens of the diastereoisomeric dimethylurea derivatives **6** and **7** of 7-ethoxy-7-isocyanatobicyclo[4.1.0]heptanes differ by 11.7 ppm. Chemical shifts upfield from internal 2-pyrrolidone can be converted to chemical shifts upfield from external ^{15}N-enriched nitric acid by addition of 259.3 ppm.[10] The stereochemical assignments of **1**–**7** were based upon the assumption that the observed differences in the ^{15}N resonances of the diastereoisomers reside predominantly in differences in steric effects at γ carbons. The stereochemistry of the major stereoisomer of analogous bicyclic systems **8** and **9** for which sufficient quantities of both diastereoisomers were not available for natural abundance ^{15}N NMR was assigned using **1**–**7** as model systems.





Our ^{15}N NMR results appear to be internally self consistent and consistent with the proposed steric nature of the γ shift. Bicyclic systems **4**–**7** and **9**, however, also bear δ substituents. The linear regression analysis of ^{15}N absorptions for acyclic amines performed by Roberts and co-workers yields a value of -3.0 ppm for δ substituents.[7] Hence the δ shift in acyclic systems is opposite in sign to the γ shift and larger in magnitude. Because the steric origin of the γ shift in ^{15}N NMR has not been completely established and because the origin and magnitude of the δ shift in more rigid systems are uncertain, we performed X-ray crystallographic analyses of the dimethylurea derivatives **5** and **8**.



Experimental Section

Crystal Data. Single crystals of the bicyclohexane derivative **5** suitable for X-ray analysis were obtained by recrystallization from the mixed solvent methylene chloride–isooctane. The crystals (mp 139.0–139.5 °C) formed as clear colorless triangular plates. A sample of dimension 0.60 × 0.56 × 0.32 mm was mounted and aligned on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromator ($2\theta_{mono}$ = 12.2°). The cell dimensions, determined on the diffractometer and refined by least-squares fit of the parameters to 15 centered reflections, are a = 8.053 (2), b = 17.251 (7), and c = 9.123 (2) Å, and β = 107.11 (2)°. The volume is 1211.3 (7) Å^3. Assuming four molecules of the compound (MW = 212.3 amu) per unit cell, the calculated density is 1.16 g/mL, in good agreement with the observed density of 1.17 g/mL measured by flotation using carbon tetrachloride and cyclohexane. From the absences observed in preliminary scans of portions of the sphere of reflection, the space group is $P2_1/n$.[11] This nonstandard setting was chosen to avoid a β angle of approximately 59°. $F(000)$ is 464.

Single crystals of the bicyclopentane derivative **8** were obtained from the mixed solvent methylene chloride–methylcyclohexane–isooctane. The crystals (mp 151.5–152.0 °C) formed as clear colorless parallelepipeds. The sample chosen had dimensions of 0.66 × 0.42 × 0.33 mm. Cell parameters, determined in the same manner as the bicyclohexane derivative, are a = 10.187 (5), b = 13.822 (7), and c = 16.207 (7) Å. The volume is 2282 (2) Å^3. Assuming eight molecules of the compound (MW = 198.3 amu) per unit cell, the calculated density is 1.15 g/mL. The measured density, obtained under the same conditions as described above, is 1.18 g/mL. The space group is *Pbca*.[12] $F(000)$ is 864.

Intensity Measurements. Intensity measurements for both samples were made using the θ–2θ scanning technique with scan rates varying from 24.0°/min for reflections with more than 1500 counts in a 2-s scan to 1.0°/min for reflections with ten counts in a 2-s scan. Reflections with less than ten counts in a 2-s scan were considered to be unobserved and were not measured. The value of ten counts was chosen by surveying background at random. The scan ranges were calculated to start 1.0° below $K_{\alpha 1}$ (λ = 0.70926) and to end 1.0° above $K_{\alpha 2}$ (λ = 0.71354).

For the bicyclohexane derivative, some 3900 reflections were scanned in a single quadrant over the range 2.0° ≤ 2θ ≤ 60.0°. Of the reflections scanned, 1798 were found to meet the criterion of ten counts in a 2-s scan and were measured. Data were processed in the usual way with values of I_0 and $\sigma(I_0)$ corrected for Lorentz and polarization effects. Of the 1798 independent points measured 1690 were determined to have intensity significantly above background and were used in the solution and refinement of the structure. A reflection was taken as significant when $F_o^2 > 3.0*\sigma(F_o^2)$ where

$$\sigma(F_o^2) = \mathrm{RLP}*[\mathrm{TSC} + \mathrm{BACK} + [P*(\mathrm{TSC} - \mathrm{BACK})]^2]^{1/2}$$

TSC is the total number of counts accumulated during the background measurements. P, a damping factor to downweight stronger intensities, was given a value of 0.04.[13] RLP, the reciprocal of the Lorentz and polarization correction, was defined as

$$\frac{2.0 \sin\theta \cos\theta}{0.5\left(\frac{\cos^2 2\theta_m + \cos^2 2\theta}{1 + \cos^2 2\theta_m}\right) + 0.5\left(\frac{\cos 2\theta_m + \cos^2 2\theta}{1 + \cos 2\theta_m}\right)}$$

where θ_{mono} is the monochromator angle.

For the bicyclopentane derivative, some 3800 reflections were surveyed within a single octant. Of these, 1072 met the ten-count criterion and were measured; 900 points were determined to be significant and were used in the solution and refinement of the structure.

Table I. Positional and Thermal Parameters for the Atoms of the Dimethylurea Derivative **5** of 6-Ethoxy-6-isocyanatobicyclo[3.1.0]hexane

atom	x^a	y	z	$B_{11}{}^b$ or B, Å^2	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0.53066 (18)	0.11301 (8)	0.37924 (16)	186.9 (29)	29.2 (5)	137.2 (22)	2.9 (10)	31.9 (20)	10.0 (9)
O(2)	0.71611 (18)	0.27218 (8)	0.44402 (16)	176.5 (29)	30.2 (5)	137.7 (22)	3.3 (10)	−18.6 (20)	−6.6 (9)
N(1)	0.51887 (21)	0.22655 (9)	0.22890 (19)	134.3 (28)	21.5 (5)	105.8 (22)	5.5 (10)	10.1 (22)	−2.7 (9)
N(2)	0.52956 (22)	0.35698 (9)	0.29176 (19)	193.0 (34)	21.8 (5)	117.4 (24)	4.3 (11)	19.6 (23)	−5.2 (9)
C(1)	0.75051 (28)	0.12285 (13)	0.25030 (28)	166 (4)	34.1 (8)	148.3 (33)	24.3 (15)	16.0 (29)	−12.0 (14)
C(2)	0.85161 (35)	0.17451 (19)	0.17343 (36)	174 (5)	58.7 (13)	234 (5)	−9.5 (22)	84 (4)	−34.4 (22)
C(3)	0.72911 (38)	0.19377 (19)	0.01586 (35)	254 (6)	52.4 (13)	204 (5)	−14.1 (22)	128 (5)	−12.4 (19)
C(4)	0.59208 (36)	0.12987 (15)	−0.02215 (29)	219 (5)	41.1 (10)	148.5 (36)	5.4 (18)	55.4 (36)	−13.4 (15)
C(5)	0.58751 (27)	0.09675 (12)	0.12925 (25)	181 (4)	26.6 (7)	137.7 (31)	7.4 (14)	27.6 (28)	−11.3 (12)
C(6)	0.57724 (24)	0.14860 (11)	0.25812 (22)	151.6 (34)	22.4 (6)	115.5 (27)	7.2 (12)	22.3 (25)	−1.1 (10)
C(7)	0.59470 (24)	0.28454 (10)	0.32887 (21)	134.1 (32)	23.0 (6)	105.0 (26)	−1.7 (12)	37.9 (24)	−3.0 (10)
C(8)	0.3828 (5)	0.37501 (17)	0.16205 (34)	320 (8)	30.6 (9)	147 (4)	20.9 (22)	−20 (4)	2.6 (16)
C(9)	0.6015 (4)	0.42067 (15)	0.39357 (35)	284 (6)	25.0 (8)	178 (4)	−3.4 (18)	29 (5)	−17.2 (14)
C(10)	0.34957 (35)	0.10241 (17)	0.35043 (34)	209 (5)	39.0 (10)	190 (4)	−10.8 (19)	50.4 (37)	9.7 (18)
C(11)	0.3132 (5)	0.08270 (21)	0.4986 (4)	312 (8)	46.0 (13)	233 (6)	12.0 (25)	134 (5)	21.9 (22)
H(1N1)	0.4330 (27)	0.2333 (11)	0.1506 (25)	0.71 (38)					
H(1C1)	0.8082 (29)	0.0916 (14)	0.3220 (28)	2.2 (5)					
H(1C2)	0.8950 (37)	0.2191 (18)	0.2346 (34)	4.2 (7)					
H(2C2)	0.956 (4)	0.1460 (17)	0.1663 (33)	4.4 (7)					
H(1C3)	0.6731 (33)	0.2472 (18)	0.0147 (29)	3.2 (6)					
H(2C3)	0.780 (4)	0.1994 (18)	−0.0681 (39)	5.2 (7)					
H(1C4)	0.4813 (33)	0.1466 (14)	−0.0847 (27)	2.2 (5)					
H(2C4)	0.6248 (33)	0.0884 (17)	−0.0774 (32)	3.8 (6)					
H(1C5)	0.5366 (28)	0.0429 (15)	0.1359 (26)	2.6 (5)					
H(1C8)	0.394 (5)	0.4266 (27)	0.136 (5)	7.7 (10)					
H(2C8)	0.382 (4)	0.3478 (21)	0.071 (4)	5.4 (8)					
H(3C8)	0.286 (7)	0.3471 (34)	0.159 (6)	9.6 (18)					
H(1C9)	0.698 (4)	0.4036 (19)	0.486 (4)	5.1 (7)					
H(2C9)	0.642 (5)	0.4592 (25)	0.339 (5)	8.0 (11)					
H(3C9)	0.511 (5)	0.4462 (26)	0.426 (5)	8.4 (11)					
H(1C10)	0.3057 (36)	0.0614 (20)	0.2753 (34)	4.9 (7)					
H(2C10)	0.2908 (38)	0.1487 (19)	0.3079 (35)	4.6 (7)					
H(1C11)	0.357 (5)	0.1265 (27)	0.567 (5)	8.2 (12)					
H(2C11)	0.188 (6)	0.0834 (25)	0.491 (4)	7.3 (10)					
H(3C11)	0.375 (4)	0.0361 (23)	0.545 (4)	5.8 (8)					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficient $\times 10^4$.

For both samples, the four reference standards monitored after every 100 reflections scanned showed no significant variation during the course of the data collection. No corrections were made for absorption, μ(Mo Kα) = 0.865 for the bicyclohexane derivative and 0.870 for the bicyclopentane derivative.

Solution and Refinement of the Structures. Both structures were solved by direct methods using the program MULTAN.[14] For the bicyclohexane derivative, phases were calculated for all 185 reflections with $|E| \geq 1.60$. An E map, generated using the phases determined in the solution with the highest figure of merit (FOM) 1.40 and the lowest residual (RES) 13.73, revealed the 15 nonhydrogen atoms in the top 16 peaks. The other peak in the top 16 corresponded to the amine hydrogen. For the bicyclopentane derivative, 307 of the 326 reflections with $E \geq 1.0$ were phased. The best solution, FOM = 1.036 and RES = 55.11, revealed the 14 nonhydrogen atoms in the top 15 peaks. The remaining peak again corresponded to a hydrogen atom. Both models were refined using full-matrix least-squares procedures assuming isotropic thermal parameters. At convergence, $R = \Sigma|\,|F_o| - |F_c|\,|/\Sigma|F_o|$ was 0.14 for the bicyclohexane derivative and 0.13 for the bicyclopentane derivative. From subsequent three-dimensional difference maps calculated for each structure, the positions of the hydrogen atoms were located. Further cycles of refinement on all parameters except the hydrogen atom temperature factors converged at $R = 0.058$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.075$ for the bicyclohexane derivative and $R = 0.044$ and $R_w = 0.057$ for the bicyclopentane derivative. The standard deviations of an observation of unit weight were 2.57 and 1.94, respectively. The ratios of observations to variables were 9 to 1 and 5 to 1, respectively. Since there were more data available for the bicyclohexane derivative, the model was refined further allowing all parameters to vary. At convergence, $R = 0.049$ and $R = 0.061$. The standard deviation of an observation of unit weight was 2.10 and the ratio of observations to variables was 8 to 1. Final difference maps on both compounds were featureless. For all calculations the scattering curves used were for neutral atoms.[15] The weighting scheme was based on counting statistics such that the weight, w, was defined as $w = 1/\sigma^2(F_o) = 4.0{*}F_o{}^2/\sigma^2(F_o{}^2)$. All programs used except for the data reduction routine were contained in or based on Ibers' Northwestern University Crystallographic Computing Package. The data reduction program was written in this laboratory and is based in part on routines supplied by Syntex Analytical Instruments.

Final positional and thermal parameters for the two molecules are given in Tables I and II. Figures 1 and 2 are ORTEP[16] drawings showing the configurations of the molecules and the numbering scheme adopted. Listings of the observed and calculated structure amplitudes are available (see paragraph at end of paper regarding supplementary material).

Data Collection Check. To check the effects of using the number of counts in a 2-s scan as a cutoff for measuring reflections, a second data set was collected for the bicyclohexane derivative using the same conditions as used previously except for the ten-count cutoff criterion. This data set resulted in 358 more observed reflections. The difference in the number of observed reflections may be attributed to our method of randomly sampling background. A better procedure would be to sample background only at high values of 2θ. This would minimize the background cutoff limit and should ensure that all significant reflections are measured.

The model was refined by least-squares procedures using this second data set and varying all parameters. At convergence the residuals, R and R_w, were 0.054 and 0.061, respectively. The positional parameters of all atoms were within 2σ of each other. The greatest shift of a nonhydrogen atom was less than 0.0006 Å. The close agreement in

Table II. Positional and Thermal Parameters for the Atoms of the Dimethylurea Derivative **8** of 5-Ethoxy-5-isocyanatobicyclo[2.1.0]-pentane

Atom	x	y	z	B_{11}[a] or B, Å^2	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0.2079 (2)	0.2355 (2)	0.4215 (1)	12.9 (3)	8.3 (2)	3.5 (1)	0.5 (2)	0.9 (1)	0.5 (1)
O(2)	0.4279 (2)	0.2170 (2)	0.2568 (1)	8.1 (3)	8.9 (2)	4.2 (1)	0.0 (2)	−0.2 (1)	−0.6 (1)
N(1)	0.2077 (3)	0.2342 (2)	0.2736 (2)	7.4 (3)	6.5 (2)	3.6 (1)	−0.3 (2)	0.3 (2)	−0.4 (1)
N(2)	0.2939 (3)	0.1623 (2)	0.1558 (2)	8.4 (3)	8.1 (2)	3.4 (1)	−0.3 (2)	−0.2 (2)	−0.9 (1)
C(1)	0.2961 (4)	0.3802 (3)	0.3544 (2)	12.0 (5)	6.3 (3)	4.4 (2)	−0.6 (3)	−0.7 (2)	−0.4 (2)
C(2)	0.2943 (4)	0.4370 (3)	0.2735 (3)	13.1 (6)	6.6 (3)	5.7 (2)	−0.9 (3)	0.0 (3)	0.5 (2)
C(3)	0.1403 (4)	0.4376 (3)	0.2760 (3)	13.7 (6)	6.6 (3)	5.8 (2)	1.0 (3)	−0.5 (3)	0.5 (2)
C(4)	0.1452 (4)	0.3825 (3)	0.3568 (2)	11.4 (5)	6.7 (3)	4.7 (2)	0.5 (3)	0.0 (2)	−1.1 (2)
C(5)	0.2172 (3)	0.2891 (3)	0.3480 (2)	9.4 (4)	6.4 (3)	3.1 (1)	−0.4 (3)	0.0 (2)	−0.3 (2)
C(6)	0.3157 (3)	0.2045 (2)	0.2301 (2)	7.7 (4)	5.5 (2)	3.5 (2)	−0.6 (2)	−0.4 (2)	0.4 (2)
C(7)	0.4041 (4)	0.1255 (4)	0.1094 (3)	12.4 (6)	10.8 (4)	4.8 (2)	0.9 (4)	0.9 (3)	−1.9 (3)
C(8)	0.1647 (4)	0.1474 (4)	0.1203 (3)	11.3 (5)	10.9 (4)	4.1 (2)	−0.7 (3)	−0.7 (3)	−0.9 (2)
C(9)	0.3135 (4)	0.1703 (4)	0.4365 (3)	16.2 (6)	8.3 (3)	4.7 (2)	1.6 (4)	0.0 (3)	0.8 (2)
C(10)	0.2828 (7)	0.1119 (5)	0.5114 (3)	26 (1)	10.6 (5)	5.6 (3)	−0.1 (6)	−0.9 (5)	2.6 (3)
H(1C1)	0.368 (4)	0.381 (3)	0.394 (3)	5.4					
H(1C4)	0.091 (4)	0.390 (3)	0.406 (3)	5.6					
H(1C2)	0.333 (4)	0.509 (4)	0.283 (3)	6.3					
H(2C2)	0.339 (4)	0.404 (3)	0.225 (3)	6.3					
H(1C3)	0.098 (4)	0.510 (4)	0.278 (3)	6.3					
H(2C3)	0.100 (5)	0.403 (3)	0.224 (3)	6.3					
H(1N1)	0.117 (4)	0.218 (3)	0.256 (2)	4.6					
H(1C9)	0.326 (4)	0.125 (4)	0.384 (3)	6.5					
H(2C9)	0.389 (5)	0.209 (4)	0.440 (3)	6.5					
H(1C7)	0.415 (5)	0.054 (3)	0.116 (3)	6.7					
H(2C7)	0.386 (5)	0.124 (4)	0.056 (3)	6.7					
H(3C7)	0.477 (5)	0.139 (4)	0.128 (3)	6.7					
H(1C8)	0.117 (5)	0.206 (4)	0.120 (3)	6.5					
H(2C8)	0.176 (4)	0.148 (4)	0.061 (3)	6.5					
H(3C8)	0.118 (5)	0.099 (4)	0.145 (3)	6.5					
H(1C10)	0.286 (6)	0.147 (5)	0.555 (4)	8.4					
H(2C10)	0.202 (5)	0.088 (4)	0.501 (4)	8.4					
H(3C10)	0.353 (5)	0.059 (4)	0.524 (3)	8.4					

[a] The form of the anisotropic thermal ellipsoid is exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^3.

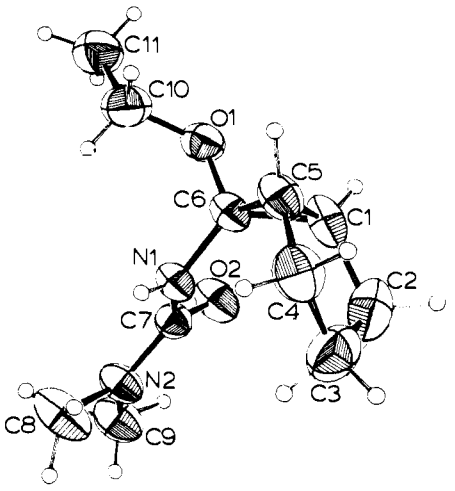


Figure 1. Perspective drawing of the dimethylurea derivative **5** of 6-ethoxy-6-isocyanatobicyclo[3.1.0]hexane. Thermal ellipsoids are represented at the 50% probability level. Hydrogen atoms are included on an arbitrary scale for clarity.

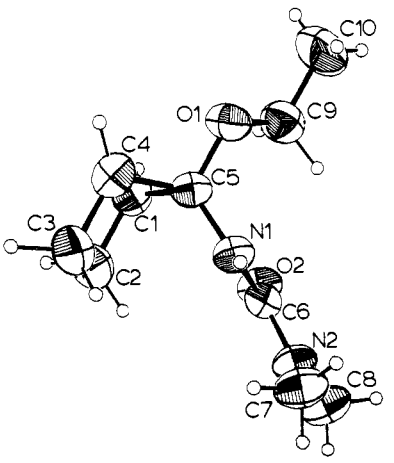


Figure 2. Perspective drawing of the dimethylurea derivative **8** of 5-ethoxy-5-isocyanatobicyclo[2.1.0]pentane. Thermal ellipsoids are drawn at the 50% probability level. Hydrogens are included on an arbitrary scale for clarity.

the results of the refinements on the two data sets indicates that skipping weak reflections had little effect on the results of the X-ray analysis and certainly did not adversely affect the analysis. All results and conclusions presented here are based on the original data set.

Results and Discussion

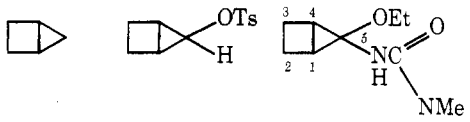
As shown in Figures 1 and 2, the X-ray structural analyses establish the stereochemistry of the bicyclohexane derivative **5** and the bicyclopentane derivative **8** as originally proposed from chemical shifts in natural abundance ^{15}N NMR spectra.[6]

Bond lengths and bond angles for the bicyclohexane and bicyclopentane derivatives are shown in Table III. Examination of the bond lengths and angles for the bicyclopentane shows very little difference between the values reported here and those obtained from microwave analysis of bicyclo[2.1.0]pentane[17]

Table III. Bond Lengths and Bond Angles for the Bicyclohexane and Bicyclopentane Derivatives **5** and **8**, Respectively

a. bond lengths, Å			
bicyclohexane derivative **5**			
O(1)-C(6)	1.408 (3)	C(1)-C(2)	1.512 (4)
O(1)-C(10)	1.416 (3)	C(1)-C(5)	1.514 (3)
O(2)-C(7)	1.225 (2)	C(1)-C(6)	1.486 (3)
N(1)-C(6)	1.424 (2)	C(2)-C(3)	1.522 (4)
N(1)-C(7)	1.370 (2)	C(3)-C(4)	1.526 (4)
N(2)-C(7)	1.359 (2)	C(4)-C(5)	1.505 (3)
N(2)-C(8)	1.439 (3)	C(5)-C(6)	1.499 (3)
N(2)-C(9)	1.445 (3)	C(10)-C(11)	1.504 (4)
bicyclopentane derivative **8**			
O(1)-C(5)	1.406 (4)	C(1)-C(2)	1.530 (5)
O(1)-C(9)	1.424 (5)	C(1)-C(4)	1.539 (5)
O(2)-C(6)	1.234 (3)	C(1)-C(5)	1.497 (5)
N(1)-C(5)	1.428 (4)	C(2)-C(3)	1.570 (6)
N(1)-C(6)	1.371 (4)	C(3)-C(4)	1.517 (6)
N(2)-C(6)	1.356 (4)	C(4)-C(5)	1.492 (5)
N(2)-C(7)	1.444 (5)	C(9)-C(10)	1.491 (7)
N(2)-C(8)	1.450 (5)		
b. bond angles, deg			
bicyclohexane derivative **5**			
C(6)-O(1)-C(10)	114.1 (2)	C(1)-C(5)-C(6)	59.1 (1)
C(6)-N(1)-C(7)	120.5 (2)	C(4)-C(5)-C(6)	121.0 (2)
C(7)-N(2)-C(8)	124.5 (2)	O(1)-C(6)-N(1)	114.2 (2)
C(7)-N(2)-C(9)	119.1 (2)	O(1)-C(6)-C(1)	112.2 (2)
C(8)-N(2)-C(9)	116.2 (2)	O(1)-C(6)-C(5)	116.4 (2)
C(2)-C(1)-C(5)	107.9 (2)	N(1)-C(6)-C(1)	122.4 (2)
C(2)-C(1)-C(6)	119.2 (2)	N(1)-C(6)-C(5)	120.5 (2)
C(5)-C(1)-C(6)	59.9 (1)	C(1)-C(6)-C(5)	61.0 (1)
C(1)-C(2)-C(3)	106.2 (2)	O(2)-C(7)-N(1)	122.0 (2)
C(2)-C(3)-C(4)	106.3 (2)	O(2)-C(7)-N(2)	121.7 (2)
C(3)-C(4)-C(5)	106.1 (2)	N(1)-C(7)-N(2)	116.2 (2)
C(1)-C(5)-C(4)	107.8 (2)	O(1)-C(10)-C(11)	109.0 (2)
bicyclopentane derivative **8**			
C(5)-O(1)-C(9)	115.3 (3)	C(3)-C(4)-C(5)	111.6 (3)
C(5)-N(1)-C(6)	122.6 (3)	O(1)-C(5)-N(1)	115.5 (3)
C(6)-N(2)-C(7)	119.1 (3)	O(1)-C(5)-C(1)	114.9 (3)
C(6)-N(2)-C(8)	124.1 (3)	O(1)-C(5)-C(4)	110.0 (3)
C(7)-N(2)-C(8)	116.7 (3)	N(1)-C(5)-C(1)	122.8 (3)
C(2)-C(1)-C(4)	89.9 (3)	N(1)-C(5)-C(4)	120.5 (3)
C(2)-C(1)-C(5)	111.4 (3)	C(1)-C(5)-C(4)	62.0 (3)
C(4)-C(1)-C(5)	58.9 (2)	O(2)-C(6)-N(1)	121.4 (3)
C(1)-C(2)-C(3)	89.6 (3)	O(2)-C(6)-N(2)	121.6 (3)
C(2)-C(3)-C(4)	89.3 (3)	N(1)-C(6)-N(2)	117.0 (3)
C(1)-C(4)-C(3)	91.2 (3)	O(1)-C(9)-C(10)	108.9 (4)
C(1)-C(4)-C(5)	59.2 (2)		
c. bond lengths involving hydrogen, Å			
bicyclohexane derivative **5**			
N(1)-H(1N1)	0.84 (2)	C(8)-H(2C8)	0.95 (4)
C(1)-H(1C1)	0.87 (2)	C(8)-H(3C8)	0.91 (6)
C(2)-H(1C2)	0.95 (3)	C(9)-H(1C9)	1.01 (3)
C(2)-H(2C2)	0.99 (3)	C(9)-H(2C9)	0.94 (4)
C(3)-H(1C3)	1.02 (3)	C(9)-H(3C9)	0.97 (4)
C(3)-H(2C3)	0.98 (4)	C(10-H(1C10)	0.98 (3)
C(4)-H(1C4)	0.95 (3)	C(10-H(2C10)	0.95 (3)
C(4)-H(2C4)	0.96 (3)	C(11)-H(1C11)	0.98 (5)
C(5)-H(1C5)	1.03 (3)	C(11)-H(2C11)	0.99 (4)
C(8)-H(1C8)	0.93 (4)	C(11)-H(3C11)	0.97 (4)
bicyclopentane derivative **8**			
N(1)-H(1N1)	1.00 (4)	C(7)-H(3C7)	0.82 (5)
C(1)-H(1C1)	0.97 (4)	C(8)-H(1C8)	0.94 (5)
C(2)-H(1C2)	1.09 (5)	C(8)-H(2C8)	0.97 (5)
C(2)-H(2C2)	1.01 (5)	C(8)-H(3C8)	0.91 (5)
C(3)-H(1C3)	1.09 (5)	C(9)-H(1C9)	1.07 (5)
C(3)-H(2C3)	1.05 (5)	C(9)-H(2C9)	0.94 (5)
C(4)-H(1C4)	0.98 (5)	C(10)-H(1C10)	0.86 (6)
C(7)-H(1C7)	1.01 (5)	C(10)-H(2C10)	0.90 (5)
C(7)-H(2C7)	0.89 (5)	C(10)-H(3C10)	1.05 (5)

Table IV. Comparison of Bond Lengths for Three Bicyclo[2.1.0]-pentane Derivatives



C(1)-C(4)	1.536 (1)[a]	1.525 (8)[b]	1.539 (5)
C(1)-C(2)	1.528 (2)	1.523 (8)	1.530 (5)
C(4)-C(3)	1.528 (2)	1.535 (8)	1.517 (6)
C(1)-C(5)	1.507 (1)	1.488 (8)	1.497 (5)
C(4)-C(5)	1.507 (1)	1.472 (8)	1.492 (5)
C(2)-C(3)	1.565 (1)	1.540 (8)	1.570 (6)

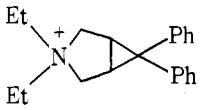
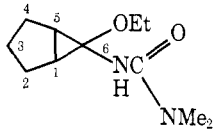
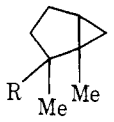
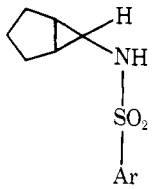
[a] Values in this column from ref 17. [b] Values in this column from ref 18.

and by X-ray analysis of *exo*-bicyclo[2.1.0]pentyl tosylate.[18] For these three compounds the bond lengths, which are compared in Table IV, are within experimental error of each other. This close agreement suggests that the cyclopropane ring, and in particular the C(1)-C(4) bond, is not strongly affected by the substituents on the ring.

Some substituent effects on the carbon-carbon bond lengths of cyclopropane have been noted and discussed in the literature in terms of σ-electron withdrawing, π-electron withdrawing, π-electron donating, and rehybridization effects.[19] Significant effects have been observed with strong σ and π electron-withdrawing substituents such as fluorine[20] and cyano,[21] respectively. Chlorine and bromine exhibit less dramatic effects.[19] Since the ethoxy and urea substituents of **5** and **8** are probably operating as moderate σ electron-withdrawing substituents, only small effects on bond lengths are predicted consistent with observation. For the bicyclohexane derivative **5**, agreement between the bond lengths obtained from this study and those obtained by a combination of microwave spectroscopy and electron diffraction analysis of bicyclo[3.1.0]hexane[22] and by X-ray analysis of various other bicyclo[3.1.0]hexyl systems[23-25] is poor. Bond lengths for the bicyclohexanes are compared in Table V. The X-ray data, with one exception, indicate that the C(1)-C(5) bridging bond is longer than that determined by a combination of microwave spectroscopy and electron diffraction and is much closer to the length of 1.509 Å found in cyclopropane[26] and to the length of 1.513 Å used by Cook and Malloy[27] for their analysis of the microwave spectrum of bicyclo[3.1.0]hexane. The one X-ray data set which does not indicate the longer C(1)-C(5) bond[25] is questionable since we were unable to reproduce the reported C(1)-C(5) bond length using the parameters given. On the basis of our X-ray study and the premise that the ethoxy and urea substituents do not have any more effect on the cyclopropane ring of the bicyclohexane derivative **5** than they do on the cyclopropane ring of the bicyclopentane derivative **8**, we conclude that the C(1)-C(5) bond length determined from a combination of microwave spectroscopy and electron diffraction is apparently in error and that the bond length is, in fact, close to the cyclopropane distance. Further evidence that the distance for the bridging bond determined in this study is accurate is the close agreement between the bond lengths and bond angles in the ethoxy and urea substituents in the bicyclopentane and bicyclohexane derivatives **8** and **5**, respectively. This agreement is within two standard deviations.

As evident from Figure 1 the bicyclo[3.1.0]hexane ring of **5** exists in a boat conformation. This is in agreement with numerous NMR studies of the conformation of the bicyclo[3.1.0]hexane ring system[28] and with the molecular structure studies described above[22,24,25] with one exception, 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexyl bromide.[23] An

Table V. Comparison of Bond Lengths for Bicyclo[3.1.0]hexanes

					
C(1)-C(5)	1.454 (9)[c]	1.525 (5)[d]	1.514 (3)	1.52 (3)[e]	1.46 (1)[a]
C(1)-C(2)	1.543 (4)	1.499 (6)	1.512 (4)	1.53 (3)	1.51
C(4)-C(5)	1.543 (4)	1.507 (6)	1.505 (3)	1.48 (3)	1.49
C(1)-C(6)	1.515 (8)	1.514 (5)	1.486 (3)	1.48 (3)	1.49
C(5)-C(6)	1.515 (8)	1.521 (5)	1.499 (3)	1.50 (3)	1.49
C(2)-C(3)	1.543 (4)	1.531 (6)[b]	1.522 (4)	1.57 (3)	1.49
C(3)-C(4)	1.543 (4)	1.523 (5)[b]	1.526 (4)	1.53 (3)	1.52

[a] The standard deviation is an estimate. Values in this column from ref 25. [b] These distances are for C–N bonds. [c] Values in this column are from ref 22. [d] Values in this column are from ref 23. [e] Values in this column are from ref 24.

Table VI. Least-Squares Planes and Deviations from Planarity

atoms	coefficients[a]	deviations[b]
	bicyclo[3.1.0]hexane derivative **5**	
C(1),C(5),C(6)	−1.812, −13.84, 5.425, −1.703	
C(2),C(3),C(4)	5.872, −9.208, −5.691, 2.407	
C(1),C(2),C(4),C(5)	4.576, −13.88, −3.021, 0.9636	C(1), 0.009 (2); C(2), −0.013 (3); C(4), 0.010 (3), C(5), −0.009 (2); C(3), −0.365; C(6), −1.165
	bicyclo[2.1.0]pentane derivative **8**	
C(1),C(4),C(5)	−0.2354, 1.344, −16.13, −5.274	
C(1),C(2),C(3),C(4)	0.2620, 11.90, 8.230, 7.523	C(1), −0.004 (4); C(2), 0.006 (5); C(3), −0.007 (5); C(4), 0.004 (4); C(5), −1.161

[a] Coefficients are given in the order *ABCD* for an equation of the form $Ax + By + Cz + D = 0.0$. The parameters x, y, and z are fractional cell coordinates. Planes were calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961). [b] Deviations Å from planarity are given with standard errors for those atoms used to calculate the planes and without for atoms projected onto the planes. No deviations are given for three-atom planes.

explanation for this conformational preference and the exception has been given by Robertson and co-workers.[24]

For the bicyclo[3.1.0]hexane derivative **5** the dihedral angles between the cyclopropane plane and the base plane atoms, C(1)-C(2)-C(4)-C(5), and between the base plane and the plane, C(2)-C(3)-C(4), are 65.0 and 23.5°, respectively. For the bicyclo[2.1.0]pentane **8** the dihedral angle between the cyclopropane plane and the cyclobutane plane is 65.0°. These values are in good agreement with those found in the literature as cited previously. Equations for the least-squares planes and the deviation from the planes are given in Table VI.

Except for a hydrogen bond between the secondary nitrogen and the carbonyl oxygen, there are no intermolecular contacts shorter than the expected van der Waals distances for either **5** or **8**. Therefore, the conformation determined from the X-ray study for each derivative most likely represents the predominant conformation which exists in solution except for possible rotation of the ethoxy group into one or the other of the two preferred staggered conformations. The two possible staggered conformations appear in Figures 1 and 2. In the bicyclopentane **8** (Figure 2) the ethyl group is proximal to the carbonyl group and in the bicyclohexane **5** (Figure 1) the ethyl group is distal to the carbonyl group.

The hydrogen bonds are the normal amide nitrogen carbonyl oxygen type. For the bicyclohexane derivative **5** the N---O distance is 2.995 (2) Å while the H---O distance is 2.16 (2) Å. The N—H---O angle is 169 (2)°. For the bicyclopentane derivative **8** the values are 2.902 (4) and 1.93 (4) Å and 163 (3)°, respectively.

The intramolecular contacts, relevant to a discussion of the

Table VII. Selected Intramolecular Contacts, Å

	(a) bicyclohexane derivative **5**		
N(1)-C(2)	3.007 (3)	N(1)-H(1C2)	3.02 (3)
N(1)-C(3)	2.983 (3)	N(1)-H(1C3)	2.63 (3)
N(1)-C(4)	3.028 (3)	N(1)-H(1C4)	3.11 (3)
N(1)-C(10)	2.926 (3)	N(1)-H(2C10)	2.54 (3)
N(1)-C(11)	4.166 (4)		
	(b) bicyclopentane derivative **8**		
N(1)-C(2)	2.938 (5)	N(1)-H(2C2)	2.82 (5)
N(1)-C(3)	2.894 (6)	N(1)-H(2C3)	2.70 (5)
N(1)-C(9)	2.986 (5)	N(1)-H(1C9)	2.63 (5)
N(1)-C(10)	4.278 (6)		

^{15}N NMR chemical shifts, around the secondary urea nitrogen atoms in the two molecules are given in Table VII. The ^{15}N NMR chemical shifts can be easily rationalized from these nonbonded interactions in terms of a sterically induced upfield γ shift and a sterically induced downfield δ shift. In both the bicyclohexane and bicyclopentane derivatives **5** and **8** the two ring carbons γ to the secondary urea nitrogen are sterically close to the nitrogen N(1). Hence a large upfield shift is predicted. A slightly larger upfield shift is, in fact, anticipated for the bicyclopentane derivative **8** than for the bicyclohexane derivative **5**, since the relevant γ-intramolecular contacts N(1)-C(2) and N(1)-C(3) are shorter for this ring system. For the bicyclohexane derivative the distance from N(1) to the δ-ring carbon C(3) is even shorter than the distances to the γ-ring carbons C(2) and C(4). This is, of course, a consequence of the boat conformation. A downfield shift is predicted from

the interaction of the δ-ring carbon with N(1). A combination of a downfield δ shift in **5** and the difference in magnitude predicted for the upfield γ shifts in **5** and **8** accounts for the observed 4.1-ppm difference in the ^{15}N resonances. In the bicycloheptane derivative **7** there are two δ-ring carbons as well as two γ-ring carbons. The magnitude of each δ shift in the bicycloheptane **7** is anticipated to be smaller than the δ shift in bicyclohexane **5** because **7** has a larger, more flexible ring system. Hence, the identity of the ^{15}N resonances of **5** and **7** is reasonable. A negligible δ effect is predicted for the bicycloheptene **9** since little steric interaction of the sp^2-hybridized carbons with the secondary urea nitrogen should exist. This is consistent with the observed chemical shift of the secondary nitrogen of **9** which is similar to the chemical shift of the secondary nitrogen of **8**.

The steric nature of the δ shift in ^{15}N NMR is also consistent with the observations of Roberts and co-workers. They have observed a significant δ shift for acyclic amines where δ-steric interaction is possible[7] and a negligible δ shift for piperidines where there is little or no δ-steric interaction.[9] There is also evidence that the δ shift in ^{13}C NMR is a sterically induced downfield shift. Stothers and co-workers have reported that a syn-axial hydroxyl group deshields a δ-methyl carbon by 2-3.5 ppm.[29]

We can conclude from these molecular structure studies that the δ shift in ^{15}N NMR spectroscopy can be a significant effect in some rigid systems such as **5** but that the γ shift is uniformly dominant and can be reliably used for stereochemical assignment.

Supplementary Material Available: Observed and calculated structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

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(12) The systematic absences for *Pbca* (no. 61) are $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$. The equivalent positions are x, y, z; $\frac{1}{2} - x, \frac{1}{2} + y, z$; $x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} + x, y, \frac{1}{2} - z$; and the additional four generated by the center of symmetry.
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