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A Chair–Boat Conformer in 2,4,6,8-Tetraphenyl-3-aza-7-thiabicyclo[3.3.1]nonan-9-one. An X-ray Diffraction Analysis of a Single Crystal of the Compound

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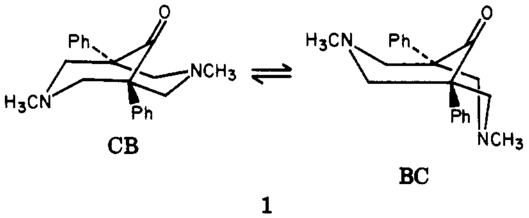
A structural analysis of 2,4,6,8-tetraphenyl-3-aza-7-thiabicyclo[3.3.1]nonan-9-one was performed via ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. An unusually large deshielding of C(1,5) (bridgehead carbons) was detected in the ^{13}C NMR spectrum and was rationalized on the basis of the deshielding influence of the phenyl rings attached to C(6,8) α to the sulfur atom. This bispidinone system is believed to exist as a chair–boat in solution (the thianone ring as a chair and the piperidone ring as a boat) as judged from spectroscopic evidence and from X-ray diffraction analysis of a single crystal of the compound. The bispidinone crystallizes as the benzene solvate in the triclinic space group $P\bar{1}$. The cell dimensions are a = 8.910 (2) Å, b = 9.754 (2) Å, and c = 19.342 (3) Å, α = 92.09 (2)°, β = 98.84 (2)°, γ = 110.75 (2)°. The system is not perfectly symmetrical and some strain is apparently in the system as evidenced by the slightly abnormally long C–C bonds involving the bridgehead carbon atoms. The nitrogen atom is pyramidal with the attached hydrogen in a pseudoequatorial position and very likely with the lone pair of electrons in a position *unfavorable* for interaction with the carbonyl carbon although the piperidone ring is a boat form. The thianone ring is in a chair form and the C(6)–C(23)–C(28) and C(8)–C(29)–C(30) bond angles [C(6) and C(8) are α to the sulfur atom] are slightly enlarged, which suggests some strain around the sulfur atom from steric interactions of sulfur with the phenyl groups.

Considerable interest in the stereodynamics and potential as useful synthons of bicyclo[3.3.1]nonan-9-one systems[1] with heteroatoms at the 3- and 7-positions[2] prompts us to reveal our findings on the stereochemistry of 2,4,6,8-tetraphenyl-3-aza-7-thiabicyclo[3.3.1]nonan-9-one. The emergence of such bicyclic systems (sometimes referred to as 3,7-diheterabispidinones) as good candidates to contain a chair–boat (CB) arrangement is recognized[2,3] but examples based on *unequivocal experimental evidence* are very rare. One example of a dynamic CB ⇄ BC system is that predicted for 1.[2d] Variable-temperature ^{1}H and ^{13}C NMR studies supported the postulate.[2c,2d] The title compound 2 might reasonably be expected to have a preferred form but heretofore no definitive evidence has been revealed to support this postulate.



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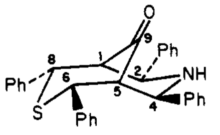
We report herein a single-crystal X-ray diffraction analysis of solid 2,[3] which exists as the CB form as also supported in a ^{13}C NMR analysis of 2 in DCCl$_3$. The ^{13}C chemical shifts (Table I) for 2 were compared with those of model compounds 3 and 4. Initially, on the basis of these comparisons and electronegatively considerations, the signal at 61.05 ppm in 2 was assigned to C(2,4) attached to the *nitrogen* atom and was remarkably similar to that (60.84 ppm) found for C(2,6) in the piperidone 3.[4] Likewise, the resonance at 52.13 ppm for C(6,8) was not sharply different from that (48.15 ppm) for C(2,6) in thianone 4. Thus, it appears that a dramatic deshielding of C(1,5) had occurred in 2 to give a signal at 59.24 ppm, quite downfield from the 50.10 and 50.24 ppm found for C(3,5) in 3 and 4, respectively. This unusual observation prompted us to prepare labeled 5 and 6, and the results will be discussed shortly.



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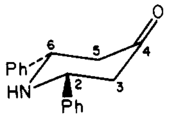

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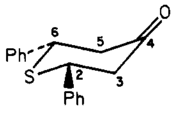

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Although bicyclo[3.3.1]nonane[1c] exists as an equilibrium CC ⇄ BC with the BC contribution increasing at higher temperatures and certain 3,7-diazabicyclo[3.3.1]nonanes appear to behave similarly,[2c] relatively few unequivocal structural assignments have appeared with the 3-aza-7-thia-substituted relatives. Not only does the current X-ray data confirm the basic structure, but the use of the deuterated analogue 5 and the ^{13}C-enriched system 6 has established a model by which other related systems may be

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[1] (a) Peters, J. A. *Synthesis* **1979**, 321. (b) Bhattacharjee, S. K.; Chacko, K. K. *Tetrahedron* **1979**, *35*, 1999. (c) Mastryukov, V. S.; Popih, M. V.; Dorofeeva, O. V.; Golubinskii, A. V.; Vilkov, L. V.; Belikova, N. A.; Allinger, N. L. *Tetrahedron Lett.* **1979**, 4339.

[2] (a) Rogozina, S. V. *Russ. Chem. Rev.* **1973**, *42*, 190. (b) Zefirov, N. S.; Rogozina, S. V. *Tetrahedron* **1974**, *30*, 2345. (c) Takeuchi, Y.; Scheiber, P.; Takada, K. *J. Chem. Soc., Chem. Commun.* **1980**, 403. (d) Takeuchi, Y.; Scheiber, P. "Abstract, 7th International Congress of Heterocyclic Chemistry", University of South Florida, Tampa, FL, Aug 12–17, **1979**, p 121.

[3] Although 2 has been reported, the procedure required 3 days. The prediction was also made that 2 could exist as a CB system; see Baliah, V.; Usha, R. *Ind. J. Chem.* **1977**, *15B*, 684.

[4] Ramalingam, K.; Berlin, K. D.; Satyamurthy, N.; Sivakumar, R. *J. Org. Chem.* **1979**, *44*, 471.

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Table I. ^{13}C NMR Chemical Shifts for the Bispidinones

compd[a]	C(2,4)	C(1,5)	C(6,8)	C(9)	Ar–C
2[b]	59.24	61.05	52.13	211.54	144.40, 137.33, 128.46, 127.94, 127.72, 127.36, 127.01, 126.53
compd[a]	C(2,6)		C(3,5)	C(4)	
3[c]	60.89		50.10	206.68	142.60, 128.36, 127.48, 126.31
4[c]	48.15		50.24	206.78	139.06, 128.43, 127.61, 126.78

[a] All data are given in parts per million downfield from Me_4Si. [b] Solution was 0.2 M in $DCCl_3$. [c] See ref 4.

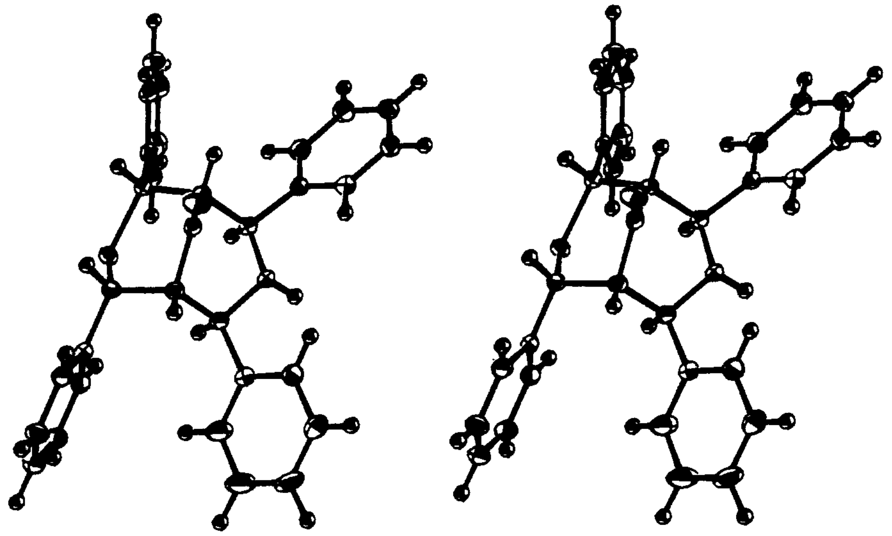
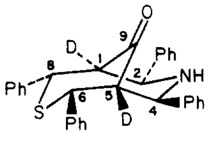
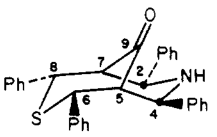


Figure 1. ORTEP drawing of single molecule of 2,4,6,8-tetraphenyl-3-azabicyclo[3.3.1]nonan-9-one (2).

compared in terms of assignments of carbon-13 resonances. The latter two compounds were prepared via a procedure identical with that for 2 with the exception that *cis*-2,6-diphenyl-3,3,5,5-tetradeuterio-4-thianone was used in the condensation to obtain **5**, and $C_6H_5{}^{13}CHO$ was employed with *cis*-2,6-diphenyl-4-thianone to synthesize **6**.





6 (• = ^{13}C)

Condensation of *cis*-2,6-diphenyl-3,3,5,5-tetradeuterio-4-thianone in the same procedure used to obtain **2** (except that absolute C_2H_5OD was employed as the solvent) gave **5**. The ^1H NMR spectrum of **5**, as expected, did *not* contain the peak for H(1,5) found at δ 3.21 in **2**, but the remaining signal patterns and shifts were essentially identical for both compounds. Interestingly, ^{13}C NMR analysis of **5** revealed signals at 59.26 ppm [C(2,4)] and 52.11 ppm [C(6,8)], while the signal at 61.05 ppm was complex and greatly diminished because of coupling to deuterium.

Synthesis of **6** involved an identical procedure as for **2** except the benzaldehyde used was diluted with benzaldehyde-α-^{13}C. Surprisingly, ^{13}C NMR analysis of **6** clearly showed the label at 59.24 ppm (Table I) for C(2,4) attached to nitrogen. Consequently, bridgehead carbons C(1,5) must have the resonance at 61.05 ppm. Quite possibly this downfield shift of C(1,5) resonance arises from deshielding imposed by the phenyl groups attached to C(6,8). The X-ray diffraction study of a crystal of **2** has indicated that the phenyl groups are not far removed from the bridgehead protons [H(1,5)] [and therefore are close to C(1,5)] since the enlarged C(6)–C(23)–C(28) angles [~123.2°) are present apparently to minimize repulsive forces between the phenyl group and the large sulfur atom.

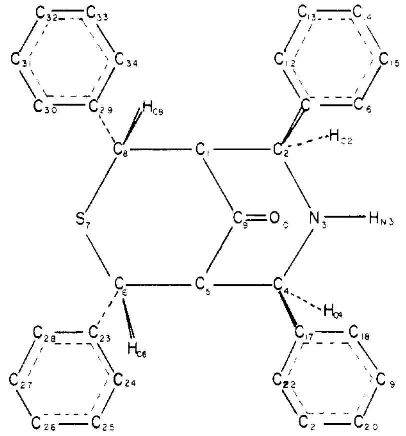


Figure 2. Schematic diagram of the molecule showing the numbering scheme used for the atoms.

Single-Crystal Analysis of 2

As shown in the ORTEP[5] drawing (Figure 1), solid bispidinone **2** was found to exist in a CB conformation with the sulfur-containing ring in a chair conformation and the nitrogen-containing ring in the boat form. For the parent molecule bicyclo[3.3.1]nonane, it has been calculated that the CC conformation is about 2.7–3.7 kcal/mol more stable that the CB conformation.[6] The molecular structure of the more closely related 2-chlorobicyclo[3.3.1]nonane-9-one also exhibits the CC conformation.[7] Zefirov and Rogozina[8]

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(5) Johnson, C. K.; ORTEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1971.

(6) Zefirov, N. S.; Rogozina, S. V. *Tetrahedron* **1974**, *30*, 2345.

(7) Webb, N. C.; Becker, M. R. *J. Chem. Soc., B* **1967**, 1317.

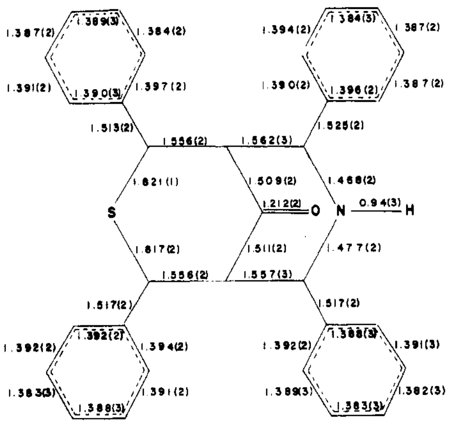
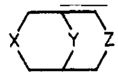


Figure 3. Bond distances in angstroms. Estimated standard deviations are shown in parentheses. Bond distances for the benzenes of solvation are available as supplementary material.

have presented arguments suggesting that when bulky heteroatoms are in the 3- and 7-positions, particularly where both are sulfur atoms, the CB conformation would be more favorable than the CC as a result of dipole–dipole repulsions, overlap of lone-pair electrons, and steric repulsions. (See Figure 2 for the numbering scheme used in the molecule.) Indeed, studies of the bicycloheterocyclic compounds revealed that 7 is a CC but 8 is a CB.[8] On this basis, with a nitrogen replacing an oxygen atom (X = N, Y = CH$_2$, Z = S), a CC system might be expected. However, in the molecule studied there is an additional factor which undoubtedly contributes to the overall stability of the CB conformation. Were this molecule to exist in the CC form, the bulky phenyl groups at carbons 2 and 4 would be in energetically unfavorable axial positions.



7, X = O; Y = Z = S
8, X = Z = S; Y = O

The bond distances for the molecule are shown in Figure 3. Bond distances and angles for the benzene molecules of solvation are available as supplementary material. The carbon–sulfur bond distance [average = 1.819 (2) Å] is comparable to the 1.817 (5) Å given by Sutton as the mean distance for paraffinic C–S bonds[9] and is within the range (1.811–1.840 Å) found in several sulfur-containing, six-membered ring systems previously studied by this group.[10,11] The carbon–nitrogen bond lengths (averge = 1.472 Å) agree with the average for paraffinic and heterocyclic C–N bonds of 1.472 (5) Å cited by Sutton.[12]

The average carbon–carbon bond distance for the C(1)–C(2), C(1)–C(8), C(4)–C(5), and C(5)–C(6) bonds is 1.558 (3) Å, long compared to a normal C–C bond distance of 1.537 (5) Å. The strain in the system indicated by this long distance is evently distributed between the bonds involved, each of which is within two standard deviations of the average. In a study of a number of bicyclo[3.3.1]nonane systems, Bhattacharjee and Chacko found for these bonds a mean distance of 1.54 (3) Å in a group of molecules having the CB conformation.[13]

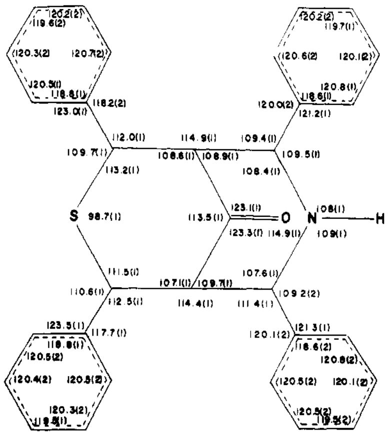


Figure 4. Bond angles in degrees. Estimated standard deviations are shown in parentheses. Bond angles for the benzenes of solvation are available as supplementary material.

Figure 4 gives the bond angles found in the compound. The nitrogen atom is definitely pyramidal with the attached hydrogen in the equatorial position, pointing away from the carbonyl group. The carbonyl grouping [C(1), C(5), C(9), and O(10)] is planar as shown by the sum of the angles around C(9) of 359.9° and by the displacement of C(9) atom from the plane formed by the other three atoms of only 0.026 Å toward the nitrogen atom. Dunitz has shown that in a number of compounds containing nitrogen atoms within 3.0 Å of carbonyl groups, there is a correlation between the distance of the nitrogen from the carbon and the displacement of the carbon from the plane of the carbonyl group.[14] In this compound, the nitrogen atom is only 2.516 (2) Å from C(9) and, according to Dunitz's calculations, if there is any appreciable interaction between them, C(9) should be displaced from the plane by approximately 0.1 Å. However, in addition to a short C–N nonbonded distance, there also appears to be a requirement for the N—C═O angle to be close to the tetrahedral angle. In this case, the angle is 131.5°. Given the pyramidal arrangement of the nitrogen atom, the lone pair of electrons on the nitrogen is undoubtedly in an orientation *unfavorable* for interaction with the carbonyl carbon atom. Therefore, it is not surprising that C(9) is only very slightly displaced from the plane.

The C(1)–C(9)–C(5) angle of 113.5 (1)° indicates that the ring system places some strain on the carbonyl group. In studying the structure of 2-chlorobicyclo[3.3.1]nonan-9-one, Webb and Baker calculated that with ideal geometry, this angle would be 116°.[7] Experimentally they measured an angle of 112°. In two similar systems, 1-methyl-7-*exo*-*tert*-butylbicyclo[3.3.1]nonan-2,9-dione[15] and D,L-1,7-(dicarbomethoxy)-3a,7-methano-3a*H*-decahydrocyclopentacyclooctane-2,10-dione,[16] this angle was determined to be 112.5 and 111.9°, respectively.

The angle between the plane formed by C(6), C(7), and C(8) and the plane formed by carbon atoms (C23) through C(28) is 23.7° with C(28) 0.47 Å below the plane [toward C(5)] and C(24) 0.49 Å above the plane. The plane formed by the carbon atoms C(29) through C(34) is tilted 29.3° with respect to the sulfur-containing plane with C(30) at 0.67 Å below the plane [toward C(1)] and C(34) at 0.50 Å above it. The phenyl groups are somewhat distorted with

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[8] Zefirov, N. S.; Rogozina, S. V. *J. Chem. Soc., Chem. Commun.* **1974**, 260.

[9] Sutton, L. E. "Tables of Interatomic Distances"; The Chemical Society: London, 1965; S 22s.

[10] Ramalingam, K.; Berlin, K. D.; Loghry, R. A.; van der Helm, D.; Satyamurthy, N. *J. Org. Chem.* **1979**, *44*, 477.

[11] Satyamurthy, N.; Sivakumar, R.; Ramalingam, K.; Berlin, K. D.; Loghry, R. A.; van der Helm, D. *J. Org. Chem.* **1980**, *45*, 349.

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[13] Bhattacharjee, S. K.; Chacko, K. K. *Tetrahedron* **1979**, *35*, 1999.

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[15] Hickmott, P. W.; Cox, F. S.; Sim, G. A., Jr. *J. Chem. Soc., Perkins Trans. 1*, **1974**, 2544.

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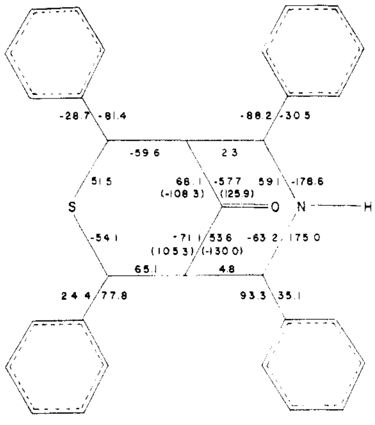


Figure 5. Selected dihedral angles. Angles for the carbonyl oxygen are shown in parentheses. Angles shown for HN(3) are those with respect to carbons C(1) and C(5).

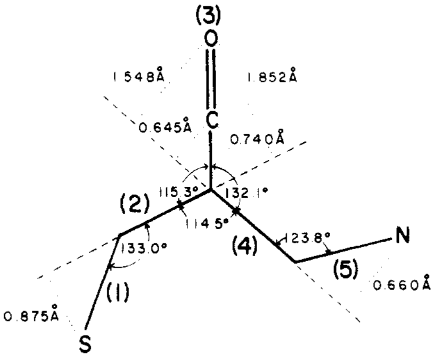
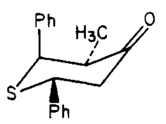


Figure 6. Angles between planes of the molecule in degrees. Dotted lines are perpendicular distances in angstroms between the atoms and indicated planes.

large C(6)–C(23)–C(28) and C(8)–C(29)–C(30) angles [average = 123.2 (1)°]. Three heterocyclic systems previously studied exhibited similar large angles: *r*-2,*t*-6-diphenyl-*c*-3-methyl-4-thianone (**9**) [average = 123.3 (3)°],[10] *r*-2-*t*-6-diphenyl-*c*-3-ethyl-4-thianone (**10**) [average = 122.9 (4)°],[10] and *cis*-2,*trans*-6-diphenyl-*cis*-3-ethylthian-*r*-4-ol (**11**) [average = 123.8 (2)].[11]



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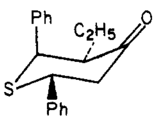

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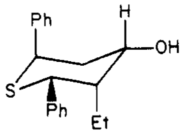

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The phenyl groups attached to C(2) and C(4) in **2** are at angles of 29.5 and 31.8°, respectively, to the plane formed by C(2), N(3), and C(4). Carbon atom C(16) is 0.67 Å above the plane [toward C(1)] and C(12) is 0.50 Å below the plane. Similarly, C(18) is 0.50 Å above the plane and C(22) is 0.77 Å below it. The angles around C(11) and C(17) are more nearly equal to 120° than those around C(23) and C(29).

The major distortions in the ring structure are shown in Figure 5, which gives the dihedral angles around the rings, and in Figure 6, which shows the angles between the various planes of the molecule. Ideal geometry for a cyclohexane ring, in the chair form, would have all of the torsion angles with an absolute magnitude of 56°. Clearly, the ring containing the sulfur atom has been flattened at the end with the sulfur atom having an average torsion angle of 52.8° and puckered at the end of the ring with the carbonyl group as shown by the average torsion angle of 69.6°. This is the opposite of the distortions seen in the structures of two thianones **9** and **10** reported earlier[9] in which the carbonyl end of the ring was flattened, having average torsion angles of 52° and 53°, respectively. The angles around the sulfur averaged 58° and 56°, respectively.

Table II. Selected Nonbonded Intramolecular Distances in 2

atoms	distance, Å (SD)
N(3)–C(9)	2.516 (2)
N(3)–O(10)	3.441 (2)
N(3)–S(7)	3.841 (1)
S(7)–C(9)	3.163 (2)
S(7)–O(10)	4.207 (1)

Table III. Summary of Crystallographic Data for 2,4,6,8-Tetraphenyl-3-aza-7-thiabicyclo[3.3.1]nonan-9-one (2)

molecular formula	$C_{31}H_{27}NOS\ 1.5C_6H_6$
molecular weight	578.8 g/mol
linear abs coeff	10.85 cm^{-1} (Cu K$\bar{\alpha}$)
density calcd	1.243 g/cm^3
space group	$P\bar{1}$
cell dimensions (138 ± 2 K)	
a, Å	8.910 (2)
b, Å	9.754 (2)
c, Å	19.342 (3)
α, deg	92.09 (2)
β, deg	98.84 (2)
γ, deg	110.75 (2)
V, Å^3	1546 ($Z = 2$)
crystal size	0.21 × 0.18 × 0.08 mm
no. of rflctns measd	5948
no. of rflctns obsd ($I > 2.5\sigma(I)$)	4797
final *R*, all rfltns	0.055
final R_w, all rfltns	0.047

Around C(9) of the nitrogen-containing ring, the average dihedral angle is 55.6°, whereas at the opposite end, the average is 61.2°. The overall result is that the C(9)–N(3) nonbonded distance of 2.52 Å is only very slightly less than would be expected in an ideal boat where the prow and stern carbons would be 2.56 Å apart. Selected nonbonded distances are listed in Table II.

As can be seen in Figure 6, the angle between planes 3 and 4 is more open at 132.1° than the 125.25° predicted for the angle between a three-membered plane and a four-membered plane in an ideal diamond-type structure.[17] The angle between planes 2 and 3 is correspondingly less, demonstrating the puckering of the sulfur-containing ring and the flattening of the nitrogen-containing ring at the carbonyl end of the rings. The 114.5° angle between planes 2 and 4 is larger than the ideal of 109.5°.

There is no evidence for any strong intermolecular hydrogen bonding. Only three nonbonded intermolecular distances between nonhydrogen and hydrogen atoms were found to be less than 2.8 Å and only one hydrogen–hydrogen distance was less than 2.4 Å.

With regard to the proximity of the phenyl rings and C(5), the system is not perfectly symmetrical. However, the C(5)–C(23) distance and the C(1)–C(29) distance do not differ significantly (2.556 Å compared to 2.544 Å, respectively). In contrast, these distances are longer than the C(5)–C(17) and C(1)–C(11) distances (2.540 Å vs. 2.521 Å), which suggests that the phenyl rings attached to C(2) and C(4) may be close enough to deshield C(1) and C(5) as reflected in the ^{13}C NMR spectrum of **2**. In contrast, the H(1)–H(34) distance was calculated to be 2.743 Å, while the H(5)–H(24) value was 2.666 Å. These distances are

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[17] Macrosson, W. D. K.; Ferguson, G. *J. Chem. Soc. B* **1968**, 242.

Table IV. Fractional Coordinates for 3-Aza-7-thia-2,4,6,8-tetraphenylbicyclo[3.3.1]nonan-9-one (Standard Deviations in Parentheses)

C(1)	−0.07631 (19)	0.30498 (17)	0.23482 (8)
C(2)	−0.17100 (19)	0.41234 (17)	0.23630 (8)
N(3)	−0.10379 (16)	0.51163 (15)	0.30152 (7)
C(4)	0.07198 (19)	0.60117 (17)	0.31039 (8)
C(5)	0.16613 (19)	0.49342 (17)	0.31463 (8)
C(6)	0.28237 (19)	0.51232 (17)	0.26036 (8)
S(7)	0.17373 (5)	0.49261 (4)	0.17082 (2)
C(8)	0.01458 (19)	0.31351 (17)	0.17163 (8)
C(9)	0.04623 (19)	0.33622 (17)	0.30210 (8)
O(10)	0.05289 (14)	0.24222 (13)	0.34048 (6)
C(11)	−0.35124 (19)	0.32385 (17)	0.23477 (9)
C(12)	−0.45675 (21)	0.27110 (19)	0.17081 (9)
C(13)	−0.61889 (21)	0.18074 (20)	0.16864 (10)
C(14)	−0.67701 (20)	0.14338 (19)	0.23041 (10)
C(15)	−0.57366 (21)	0.19801 (19)	0.29452 (10)
C(16)	−0.41198 (20)	0.28700 (18)	0.29670 (9)
C(17)	0.12172 (20)	0.70608 (18)	0.37677 (9)
C(18)	0.05187 (21)	0.66534 (20)	0.43584 (9)
C(19)	0.10070 (24)	0.76129 (22)	0.49693 (10)
C(20)	0.22394 (27)	0.89740 (22)	0.50027 (11)
C(21)	0.29602 (28)	0.93822 (21)	0.44203 (11)
C(22)	0.24510 (25)	0.84372 (20)	0.38052 (10)
C(23)	0.42705 (19)	0.65690 (17)	0.27525 (8)
C(24)	0.55510 (20)	0.66689 (18)	0.32904 (8)
C(25)	0.69023 (21)	0.79716 (19)	0.34601 (9)
C(26)	0.69955 (21)	0.91856 (19)	0.30914 (10)
C(27)	0.57248 (22)	0.90958 (18)	0.25597 (10)
C(28)	0.43689 (20)	0.77961 (18)	0.23896 (9)
C(29)	−0.10157 (18)	0.27224 (17)	0.10190 (8)
C(30)	−0.13139 (20)	0.37596 (18)	0.06012 (9)
C(31)	−0.24093 (21)	0.33144 (20)	−0.00324 (9)
C(32)	−0.32204 (22)	0.18282 (21)	−0.02526 (9)
C(33)	−0.29256 (22)	0.07857 (19)	0.01615 (10)
C(34)	−0.18340 (20)	0.12283 (18)	0.07914 (9)
C(35)	0.09435 (27)	0.21387 (24)	0.83557 (14)
C(36)	0.02893 (31)	0.18592 (26)	0.89326 (19)
C(37)	0.12479 (46)	0.23418 (29)	0.95853 (18)
C(38)	0.29356 (40)	0.31298 (28)	0.96436 (13)
C(39)	0.35842 (25)	0.34139 (23)	0.90291 (13)
C(40)	0.25720 (26)	0.29171 (22)	0.83980 (11)
C(41)	0.54247 (25)	0.37893 (22)	0.48755 (10)
C(42)	0.66182 (22)	0.51727 (23)	0.50582 (9)
C(43)	0.61966 (24)	0.63774 (21)	0.51822 (10)

shorter than either the H(5)–H(18) (3.039 Å) or H(5)–H(22) (3.239 Å) distances. Consequently, the phenyl rings attached to C(6) and C(8) may be close enough to deshield C(1,5).

Experimental Section

***cis*-2,4,6,8-Tetraphenyl-3-aza-7-thiabicyclo[3.3.1]nonan-9-one (2).** A mixture of 1.34 g (0.005 mol) of *cis*-2,6-diphenyltetrahydrothiapyran-4-one,[3] 1.06 g (0.01 mol) of benzaldehyde, 0.4 g (0.005 mol) of ammonium acetate, and 95% ethanol (10 mL) was slowly heated to 60 °C and stirred under N_2 for 5 h. The resulting mixture was cooled and 10 mL of ether was added to keep the resinous material in solution. The solution was cooled to 0 °C, and a white solid that separated was filtered off and washed with ether. This solid was recrystallized (C_6H_6) to give 0.4 g (17%) of 1: mp 207–209 °C (lit.[3] mp 207–209 °C); IR (KBr) 1710 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.50 (s, 1 H, NH), 3.21 [t, 2 H, H(1), H(5)], 4.66 [d, 2 H, J = 2 Hz, H(6), H(8)], 4.90 [d, 2 H, J = 4 Hz, H(2), H(4)], 6.76–7.49 (m, 29 H, ArH). Mass spectral peak matching for $C_{31}H_{27}NOS$ gave m/e (M^+) 461.1813, found 461.1827.

3-Aza-7-thia-2,4,6,8-tetraphenyl-1,5-dideuteriobicyclo[3.3.1]nonan-9-one (5). A mixture of 0.1 g (0.37 mmol) of *cis*-2,6-diphenyl-3,3,5,5-tetradeuterio-4-thianone,[10] 0.08 g (0.75 mmol) of benzaldehyde, 0.029 g (0.38 mmol) of ammonium acetate, and absolute C_2H_5OD (99.5% D) (1 mL) was heated to 60 °C and stirred under N_2 for 12 h. The resulting mixture was cooled, and 2 mL of diethyl ether was added to keep the resinous material in solution. The solution was cooled to 0 °C, and a white solid that separated was filtered off and washed with ether. This solid was recrystallized (C_6H_6) to give 23 mg (12%) of 5: mp 207–209 °C; IR (KBr) 1710 cm^{-1} (C=O); ^1H NMR ($DCCl_3$) δ 1.50 (s, 1 H, NH), 4.66 [s, 2 H, H(6), H(8)], 4.90 [s, 2 H, H(2), H(4)], 6.76–7.49 (m, 29 H, ArH); ^{13}C NMR ($DCCl_3$) δ 52.11 [s, C(6,8)], 59.26 [s, C(2,4)], approximately 61.05 [m, C(1,5)]. The deuterium-labeled compound 5 had a calculated m/e (M^+) for $C_{31}H_{25}D_2NOS$ of 463.1939, found 463.1976.

3-Aza-7-thia-2,4,6,8-tetraphenylbicyclo[3.3.1]nonan-9-one-*2,4*-^{13}*C* (6). A mixture of 0.2 g (0.7 mmol) of *cis*-2,6-diphenyltetrahydrothiapyran-4-one[3] and 0.058 g (0.7 mmol) of ammonium acetate in 2 mL of absolute ethanol was prepared. To the above, 0.158 g (1.5 mmol) of benzaldehyde (which contained 30.8 mg of 43.86% $C_6H_6{}^{13}CHO$) was added, and the resulting mixture was heated to 60 °C with stirring under N_2 for 12 h. Upon cooling, 2 mL of dry ether was added to keep the resinous material in solution. The solution was cooled to 0 °C, and a white solid that separated was filtered off and washed with ether. This solid was recrystallized (C_6H_6) to give 68 mg (19%): mp 207–209 °C; IR (KBr) 3320 cm^{-1} (NH), 1710 cm^{-1} (C=O). The NMR analyses (^1H and ^{13}C) gave identical results as found with 2, except in the ^{13}C NMR spectrum the signal at 59.24 ppm [C(2,4)] was greatly enhanced. The presence of the isotopic labels was observed by mass spectral analysis. Peak matching for $C_{31}H_{27}NOS$ gave m/e (M^+) 461.1813, found 461.1827, with no observed (M^+ + 1). Peak matching for the ^{13}C-labeled compound, $C_{31}H_{27}NOS$ (unlabeled), gave m/e (M^+) 461.1813, found 461.1815, and $^{13}C^{12}C_{30}H_{27}NOS$ (labeled) gave m/e (M^+) 462.1847, found 462.1876.

Crystallographic Data. Ketone 2 was recrystallized from benzene by slow evaporation and formed relatively thin prismatic crystals belonging to the triclinic system space group $P\bar{1}$. The unit cell dimensions (see Table III) and intensity data were obtained with an Enraf-Nonius CAD-4 diffractometer fitted with a low-temperature apparatus. The crystals went to powder when kept dry at room temperature for more than 2 or 3 days. Therefore, a suitable crystal was mounted directly from benzene and placed immediately (within 2–3 min) in the cold N_2 stream (138 ± 2 K) on the diffractometer.

The cell parameters were obtained by a least-squares fit ot the $\pm 2\theta$ and -2θ values of 44 reflections at 138 ± 2K, using Cu Kα_1 (λ = 1.5405 Å) radiation. The intensity data for all reflections with $2° \le 2\theta \le 150°$ were measured by using Cu K_α radiation (λ = 1.5418 Å) and the θ–2θ scan technique. The angular scan width was variable and taken to be $(1.0 + 0.35 \tan \theta)°$. A receiving aperture with a variable width of $(3.0 + 0.86 \tan \theta)$ mm and a constant height of 6 mm was located at a distance of 173 mm from the crystal. The maximum scan time for a reflection was 50 s. For each reflection, two thirds of the scan time was spent scanning the peak and one-sixth was spent scanning each of the two backgrounds. During the intensity measurements, the intensities of three standard reflections were monitored after every 3000 s of X-ray exposure time and indicated no appreciable decomposition of the crystal. A total of 5948 unique reflections was measured of which 1151 were considered unobserved having intensities less than 2.5 $\sigma(I)$. All intensity data were corrected for Lorentz and polarization factors and numerical absorption corrections were applied (μ = 10.85 cm^{-1}).

The structure was determined by direct methods using the program SHELX.[18] The phases of 380 reflections having a normalized structure factor (E) greater than 1.4 were used to construct E maps. The map with the highest reliability factor (parachor = 2.14) gave the entire structure among the top 40 peaks with the exception of three carbon atoms of the bispidinone molecule. The map also showed a benzene molecule of solvation in the asymmetric unit. After isotropic refinement of the nonhydrogen atoms found in the initial E map, the remaining three carbons of the structure were located in difference maps. An additional benzene of solvation was found around the center of symmetry, giving a total of 1.5 benzene molecules per asymmetric unit. The nonhydrogen atoms were refined by least-squares methods in

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(18) Sheldrick, G. M. SHELX-76, University Chemical Laboratory: Cambridge, 1976.

stages with isotropic and anisotropic thermal parameters. Difference maps were used to locate the hydrogen atoms, which were then refined with isotropically thermal parameters.

Because of the size of the structure and limitations in computer core space, the least-squares refinements were carried out by a blocked full-matrix method, using the computer program SHELX. The scattering factors were taken from the "International Tables", Vol. 4, pp 99 and 149. The weighting scheme used was $W_F = K/(\sigma_F)^2$, where $\sigma_F = {}^1/_2[\{\sigma^2 + (0.04P)^2]/[(P)(L_p)]\}^{1/2}$ and $\sigma = T^{1/2}\upsilon$, where υ = scan speed, $T = P_k + 4(R + L)$, $P = [P_k - 2\,(R + L)]\upsilon$, P_k = peak height, R = right background, L = left background, L_p = Lorentz and polarization. The factor K was redetermined after each structure factor calculation and was 0.134 after the final cycle of refinement.

The variance was calculated as shown by

$$\upsilon = \{M\sum[W_F(|F_o| - |F_c|)^2]/N\sum W_f\}^{1/2}$$

where N is the number of reflections in a group, M is the total number of reflections, the sum in the numerator is over all the reflections in a group, and the sum in the denominator is over all the reflections. An analysis of the variance in terms of the parity of the reflection indices, sin θ, and $[F_o/F_{max}]^{1/2}$ showed no significant variation of υ for various ranges of the functions tested. Refinement was terminated when all parameter shifts were less than 0.075 of their corresponding standard deviations. The final value of R for all 5948 reflections was 0.055 and for R_W, where $R_W = \sum W_F^{1/2}[|F_o| - |F_c|]/\sum W_f^{1/2}|F_o|$ was 0.047. The final positional parameters are given in Table IV.

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Registry No. 2, 78737-62-9; *cis*-2,6-diphenyltetrahydrothiapyran-4-one, 18456-44-5.

Supplementary Material Available: Hydrogen atom parameters, anisotropic thermal parameters, and molecular dimensions of the benzene molecules of solvation (5 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Rearrangement of [5.*n*.2]Propella-ε-lactones

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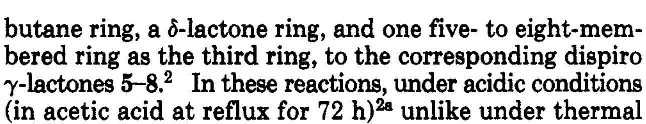
The acid-catalyzed rearrangement of [5.3.2]- and [5.4.2]propella-ε-lactones **9** and **10** in boiling acetic acid takes place readily to afford the 1,2-disubstituted cyclopentene **21** and cyclohexene **26** as the major products, respectively, while such lactone ring cleavage of the [4.3.2]- and [4.4.2]propella-δ-lactones **1** and **2** does not occur at all under similar conditions. The remarkable distinction in reactivity in the acid-catalyzed rearrangement between the ε-lactones and the δ-lactones is attributed to the effect of lactone ring size.

In a continuation of the studies on the transformation of readily available [*n*.3.2]propellanes into other important polycarbocyclic ring systems,[1] we reported the first example of the cyclobutyl–cyclopropylcarbinyl rearrangement of some propella-δ-lactones, **1–4**, composed of a cyclobutane ring, a δ-lactone ring, and one five- to eight-membered ring as the third ring, to the corresponding dispiro γ-lactones **5–8**.[2] In these reactions, under acidic conditions (in acetic acid at reflux for 72 h)[2a] unlike under thermal conditions,[2b] only [4.4.2]propella-δ-lactone **2** rearranged to give the dispiro γ-lactone **6**. This remarkable distinction of propella-δ-lactones **1–4** in reactivity toward acid could be explained on the basis of the steric effect of the third ring. Namely, it was inferred that the steric effect of the third ring reinforced the puckered geometry of the cyclobutane ring in the δ-lactones which was desirable for the rearrangement to the γ-lactones. In particular, this was the case in **2** because of the steric requirement of the cyclohexane ring to adopt the chair conformation.

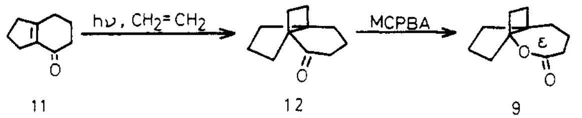


	n	
1	3	**5**
2	4	**6**
3	5	**7**
4	6	**8**

As an extension of the above reaction, we describe here the acid-catalyzed rearrangement involving the lactone ring cleavage of [5.3.2]- and [5.4.2]propella-ε-lactones **9** and **10**, higher homologues of the δ-lactones **1** and **2**, leading to the 1,2-disubstituted cyclopentene **21** and cyclohexene **26**, respectively. In addition, it is emphasized that the effect of lactone ring size, rather than the steric factor of the third ring, is the dominant factor in the present rearrangement.

Results and Discussion

The ε-lactone **9** was prepared in a manner[2b] similar to that for the δ-lactones: photocycloaddition of bicyclo[4.3.0]non-1(6)-en-2-one (**11**) to ethylene (91%), followed by the Baeyer–Villiger oxidation of the propellanone **12** with *m*-chloroperbenzoic acid (MCPBA) in chloroform.



11 **12** **9**

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