

A Conformational Process in the Solid State. Characterization of a Cyclohexanone Chair \rightleftharpoons Boat Interconversion in Derivatives of Bicyclo[3.3.1]nonan-9-one by X-ray Crystal Structure Analyses at Several Temperatures

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Abstract

Bicyclo[3.3.1]nonan-9-one *p*-toluenesulfonylhydrazone and *p*-methoxybenzenesulfonylhydrazone undergo chair–chair (*cc*) \rightleftharpoons chair–boat (*cb*) interconversion in the solid state. X-ray studies on single crystals at temperatures in the range 130–293 K show that at the lowest temperatures the crystal structures are ordered with only the *cc* conformer present, whereas at higher temperatures the crystal structures are disordered with both *cc* and *cb* conformers present. The amount of the *cb* conformer increases as the temperature is raised, reaching 31% for the *p*-toluenesulfonyl derivative and 21% for the *p*-methoxybenzenesulfonyl derivatives at 293 K, with ΔH° for the *cc* \rightleftharpoons *cb* equilibrium in the crystal being *ca* 6 kJ mol⁻¹ for the *p*-toluenesulfonyl derivative and *ca* 12 kJ mol⁻¹ for the *p*-methoxybenzenesulfonyl derivative. Crystal data: *p*-toluenesulfonyl derivative, C₁₆H₂₂N₂O₂S, *M_r* = 306.46, triclinic, *P* $\bar{1}$, *Z* = 2; at 130 K, *a* = 7.530 (2), *b* = 10.510 (2), *c* = 11.224 (3) Å, α = 103.47 (2), β = 103.04 (3), γ = 108.51 (3)°, *V* = 774.7 (8) Å³, *D_x* = 1.31 Mg m⁻³, *R* = 0.047 for 2150 independent reflections with *I* > 2.5σ(*I*); at 293 K, *a* = 7.408 (2), *b* = 10.428 (2), *c* = 11.537 (2) Å, α = 104.31 (2), β = 102.85 (3), γ = 104.82 (3)°, *V* = 795.1 (8) Å³, *D_x* = 1.28 Mg m⁻³, *R* = 0.045 for 2710 independent reflections with *I* > 2.5σ(*I*). *p*-Methoxybenzenesulfonyl derivative, C₁₆H₂₂N₂O₃S, *M_r* = 322.46, triclinic, *P* $\bar{1}$, *Z* = 2; at 145 K, *a* = 7.279 (2), *b* = 10.181 (3), *c* = 11.951 (2) Å, α = 108.50 (2), β = 97.99 (2), γ = 104.69 (2)°, *V* = 788.8 (8) Å³, *D_x* = 1.36 Mg m⁻³, *R* = 0.041 for 2415 independent reflections with *I* > 2.5σ(*I*); at 293 K, *a* = 7.389 (1), *b* = 10.534 (2), *c* = 11.956 (2) Å, α = 107.80 (2), β = 99.29 (2), γ = 106.69 (2)°, *V* = 816.4 (8) Å³, *D_x* = 1.31 Mg m⁻³, *R* = 0.061 for 2912 independent reflections with *I* > 2.5σ(*I*).

Introduction

The study of conformational processes in liquid or vapour phases is a major theme of contemporary

chemistry (Eliel, Allinger, Angyal & Morrison, 1965; Chiurdoglu, 1971; Riddell, 1980). The related topic of conformational processes in solids, on the other hand, has received little attention.

Substantial atomic displacements are known to occur in solids, *e.g.* in photochemical reactions (Nakanish, Jones, Thomas, Hursthouse & Motevalli, 1980) and several X-ray studies have dealt with the re-orientation of molecules in single crystals (Hazell, Hazell & Larsen, 1986; Woehler, Wittebort, Oh, Kambara, Hendrickson, Inniss & Strouse, 1987; Oh, Wilson, Hendrickson, Woehler, Wittebort, Inniss & Strouse, 1987). In the case of protein crystal structures it is widely recognized that a static view of the molecules is inadequate and that significant torsional fluctuations occur (McCammon & Karplus, 1983; Cooper, 1984). Indications of atomic movements altering molecular structure in solids have come from NMR investigations (Yannoni, 1982; Lyerla, Yannoni & Fyfe, 1982; Frydman, Olivieri, Diaz, Frydman, Morin, Mayne, Grant & Adler, 1988). The ¹³C NMR spectrum of naphthazarin, for example, shows an intramolecular hydrogen-exchange process O—H...O \rightleftharpoons O...H—O; in solution the equilibrium cannot be frozen out whereas in the solid state the process is slowed appreciably at low temperatures (Shiau, Duesler, Paul, Curtin, Blann & Fyfe, 1980). Recently, hydrogen exchange between nitrogen and oxygen atoms in the 1-arylozo-2-naphthols (Olivieri, Wilson, Paul & Curtin, 1989) and the Cope rearrangement of some semibullvalene derivatives (Jackman, Benesi, Mayer, Quast, Peters, Peters & von Schnering, 1989) have been investigated by a combination of X-ray diffraction and solid-state NMR studies. Nevertheless, in marked contrast to the plethora of NMR measurements of conformational processes in liquids (Berg & Sandström, 1986, 1987), analogous results for conformational interconversions of small molecules in solids are lacking (Belton, Tanner & Wright, 1986; Klinowski, 1987).

In a review of the use of atomic vibration tensors and variation of molecular geometry in different crystal environments (structure correlation), Bürgi &

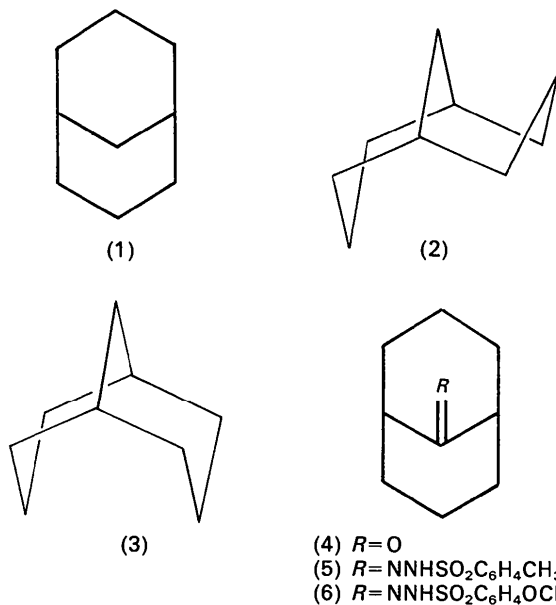
Dunitz (1983) have noted the difficulty of providing any estimate of the energy terms involved. The distribution of lengths of hydrogen bonds in crystal structures of nucleic acid components (Lesyng, Jeffrey & Maluszynska, 1988) and the distortions observed in furanose rings (Bartenev, Kameneva & Lipanov, 1987) have been employed in attempts to derive quantitative energy relationships by statistical analyses of structural parameters from different crystal environments; it has been argued, however, that the Boltzmann distribution cannot properly be applied to structural results from an assortment of crystal structures and that the results claimed have to be discounted (Bürgi & Dunitz, 1988). In a valid application of Boltzmann statistics, the temperature-dependent geometry of the pseudo-Jahn-Teller complex $[(\text{Cu}(\text{bpy})_2(\text{ONO}))\text{NO}_3]$ has been analysed in terms of two non-equivalent ground-state minima and the energy difference between these minima found to be *ca* 1 kJ mol⁻¹ (Simmons, Hathaway, Amornjarusiri, Santarsiero & Clearfield, 1987). The necessary condition for the proper application of the Boltzmann distribution is that there is a closed system at thermal equilibrium, and for such a system a convenient and conventional route for the determination of an energy (and entropy) change is provided by the variation of an equilibrium constant with temperature. A dynamic conformational equilibrium in a single crystal will result in a disordered crystal structure and determination of the partial occupancies of the alternative sites will give the equilibrium constant for the process. The statistical thermodynamic treatment of two interconverting but distinguishable systems provides the standard relation between the equilibrium constant and the free-energy change for the interconversion process in the solid.

Inversion of configuration at tertiary nitrogen atoms of organic molecules has been extensively studied in gases and liquids (Cazzoli & Lister, 1973; Lister, Tyler, Høg & Larsen, 1974; Anet & Yavari, 1977; Nelsen, 1978; Anet, 1985; Lunazzi & Macciantelli, 1985). The barriers to nitrogen inversion in six-membered rings are small and it has been estimated that the inversion process in liquids cannot be frozen out above *ca* 120 K (Katritzky, Patel & Riddell, 1980; Crabb & Katritzky, 1984). In a study of nitrogen inversion in the solid state, where barriers are expected to be substantially higher than in solution, X-ray crystal structure analyses of 1,3,5-tribenzyl-1,3,5-triazacyclohexane at several temperatures established that there is a single conformation below *ca* 250 K but above this temperature the occupations of the axial and equatorial sites at the N change with temperature, demonstrating dynamic nitrogen inversion with concomitant axial \rightleftharpoons equatorial interconversion in the solid; from the

X-ray results the enthalpy differences between the equatorial and axial sites were estimated to be 36–54 kJ mol⁻¹ (Sim, 1987).

The chair \rightleftharpoons boat interconversion of cyclohexane rings is of fundamental relevance to organic chemistry but in considering the possibility of observing the process it has to be noted that the skew boat form of cyclohexane is less stable than the chair form by *ca* 20 kJ mol⁻¹ (Eliel, Allinger, Angyal & Morrison, 1965; Squillacote, Sheridan, Chapman & Anet, 1975) and the equilibrium concentration of non-chair forms is vanishingly small at normal temperatures. It is evident that a variable-temperature X-ray study of a simple cyclohexane derivative is unlikely to provide evidence of the chair \rightleftharpoons boat interconversion in the solid and numerous X-ray studies of cyclohexane derivatives at room temperatures show conformationally ordered rings. For bicyclo[3.3.1]nonane (1), the chair-boat (*cb*) conformation (2) is less stable than the chair-chair (*cc*) conformation (3) by 10–13 kJ mol⁻¹ (Appleton, Egan, Evans, Graham & Dixon, 1968; Marvell & Knutson, 1970; White & Bovill, 1977; Osawa, Aigami & Inamoto, 1979) and the greater accessibility of a boat ring in this case is supported by an electron-diffraction study of the vapour that found *ca* 5% of the *cb* conformer at 338 K and *ca* 25% at 673 K (Mastryukov, Popik, Dorofeeva, Golubinskii, Vilkov, Belikova & Allinger, 1981). As expected from these results, X-ray studies of bicyclo[3.3.1]nonane derivatives at room temperature provide no evidence of *cb/cc* conformational disorder. For a further move towards accessibility of a boat form, the boat/chair energy difference for cyclohexanone is smaller than that for cyclohexane by *ca* 6 kJ mol⁻¹ (Allinger, Tribble & Miller, 1972) and, accordingly, the *cb/cc* energy difference for bicyclo[3.3.1]nonan-9-one (4) should be distinctly less than that for bicyclo[3.3.1]nonane (1), perhaps *ca* 4–7 kJ mol⁻¹. NMR studies of bicyclo[3.3.1]nonan-9-one in solution in carbon tetrachloride indicated that there is 22% of the *cb* form at room temperature (Raber, Janks, Johnston & Raber, 1980), a considerably higher content than that of bicyclo[3.3.1]nonane and consistent with a *cb/cc* energy difference of *ca* 5 kJ mol⁻¹. Derivatives of bicyclo[3.3.1]nonan-9-one could therefore provide examples of chair \rightleftharpoons boat interconversion in the solid state. Examination of published results showed that the crystal structure of a derivative of bicyclo[3.3.1]nonan-9-one, albeit heavily substituted at C(1), C(2) and C(5), has been reported to consist of a disordered mixture of 80% of the *cc* conformation and 20% of the *cb* conformation at room temperature (Danishefsky, Hatch, Sax, Abola & Pletcher, 1973). A preliminary X-ray survey of several 9-substituted bicyclo[3.3.1]nonan-9-one compounds in our laboratories also yielded examples of crystallo-

graphic disorder at room temperature, indicating the possibility of a conformational process in the solid, and the *p*-toluenesulfonylhydrazone (5) and *p*-methoxybenzenesulfonylhydrazone (6) were selected for detailed crystallographic investigation at several temperatures.



Experimental

Derivatives were prepared from bicyclo[3.3.1]nonan-9-one by standard procedures (Vogel, 1978). Crystallographic data for compounds (5) and (6) are listed in Tables 1 and 2; both compounds are triclinic, space group $P\bar{1}$.

p-Toluenesulfonyl derivative (5). Colourless crystals, dimensions $0.2 \times 0.3 \times 0.5$ mm. Enraf-Nonius diffractometer. At 293 K, $Mo K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 10–14°. 3732 intensities surveyed in range θ 1.5–27°, h 0→9, k -12→12, l -13→13; scan width $(1.0 + 0.25\tan\theta)^\circ$; maximum counting time 120 s; 3459 independent intensities, 2710 with $I > 2.5\sigma(I)$, $R_{int} = 0.018$. At 130, 230 and 250 K, $Cu K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 18–24°. At 250 K, 3254 reflections scanned in range θ 2–70°, h 0→9, k -12→12, l -14→14; scan width $(1.0 + 0.3\tan\theta)^\circ$; maximum counting time 120 s; 2989 independent reflections, 2712 with $I > 2.5\sigma(I)$, $R_{int} = 0.024$. At 230 K, 3006 reflections scanned in range 2–70°, h 0→9, k -12→12, l -13→13; scan width $(1.0 + 0.3\tan\theta)^\circ$; maximum counting time 120 s; 2973 independent reflections, 2750 with $I > 2.5\sigma(I)$, $R_{int} = 0.020$. At 130 K, 2370 reflections scanned in range 2–70°, h 0→5, k -12→12, l -13→13; scan width

Table 1. Crystallographic results for bicyclo[3.3.1]nonan-9-one *p*-toluenesulfonylhydrazone (5)

	130 K	230 K	250 K	293 K
a (Å)	7.530 (2)	7.458 (2)	7.425 (2)	7.408 (2)
b (Å)	10.510 (2)	10.390 (2)	10.388 (3)	10.428 (2)
c (Å)	11.224 (3)	11.369 (2)	11.454 (3)	11.537 (2)
α (°)	103.47 (2)	103.66 (2)	103.99 (2)	104.31 (2)
β (°)	103.04 (3)	103.04 (3)	102.91 (3)	102.85 (3)
γ (°)	108.51 (3)	105.76 (3)	104.90 (3)	104.82 (3)
V (Å ³)	774.7 (8)	783.3 (8)	789.1 (8)	795.1 (8)
D_x (Mg m ⁻³)	1.31	1.30	1.29	1.28
R	0.047	0.049	0.051	0.045
wR	0.075	0.071	0.073	0.063

Table 2. Crystallographic results for bicyclo[3.3.1]nonan-9-one *p*-methoxybenzenesulfonylhydrazone (6)

	145 K	220 K	250 K	293 K
a (Å)	7.279 (2)	7.285 (2)	7.298 (2)	7.389 (1)
b (Å)	10.181 (3)	10.250 (3)	10.330 (3)	10.534 (2)
c (Å)	11.951 (2)	12.020 (2)	12.042 (3)	11.956 (2)
α (°)	108.50 (2)	108.65 (2)	108.56 (2)	107.80 (2)
β (°)	97.99 (2)	98.03 (2)	98.31 (2)	99.29 (2)
γ (°)	104.69 (2)	104.79 (3)	105.14 (2)	106.69 (2)
V (Å ³)	788.8 (8)	797.9 (8)	804.6 (8)	816.4 (8)
D_x (Mg m ⁻³)	1.36	1.34	1.33	1.31
R	0.041	0.054	0.061	0.061
wR	0.079	0.077	0.087	0.093

$(1.0 + 0.3\tan\theta)^\circ$; maximum counting time 120 s; 2212 independent reflections, 2150 with $I > 2.5\sigma(I)$, $R_{int} = 0.035$; a diffractometer failure during data collection caused measurements to be restricted to h 0→5 rather than 0→9.

p-Methoxybenzenesulfonyl derivative (6). Colourless crystals, dimensions $0.25 \times 0.4 \times 0.5$ mm. Enraf-Nonius diffractometer, $Cu K\alpha$ radiation. Cell dimensions from setting angles of 25 independent reflections with θ 17–24°. At 293 K, 3502 intensities surveyed in range 1.5–72°, h 0→8, k -12→12, l -13→13; scan width $(1.0 + 0.2\tan\theta)^\circ$; maximum counting time 120 s; 3236 independent intensities, 2912 with $I > 2.5\sigma(I)$, $R_{int} = 0.040$. At 145 K, 2725 reflections scanned in range 1.5–70°, h 0→7, k -12→12, l -13→13; scan width $(1.2 + 0.2\tan\theta)^\circ$; maximum counting time 120 s; 2465 independent intensities, 2415 with $I > 2.5\sigma(I)$, $R_{int} = 0.022$. At 250 K, 3061 reflections scanned in range 2–70°, h 0→7, k -12→12, l -13→13; scan width $(1.2 + 0.2\tan\theta)^\circ$; maximum counting time 120 s; 3048 independent intensities, 2873 with $I > 2.5\sigma(I)$. At 220 K, 2004 reflections scanned in range 2–70°, h 0→4, k -12→12, l -13→13; scan width $(1.2 + 0.2\tan\theta)^\circ$, maximum counting time 120 s; 1993 independent intensities, 1916 with $I > 2.5\sigma(I)$; the crystal fractured during data collection and intensity measurements were thereby restricted to h 0→4, rather than 0→7.

Two reference reflections monitored periodically showed only a very slight variation in intensity (ca 2%) during each data collection.

The structures were elucidated by direct phasing using *MITHRIL* (Gilmore, 1984). At 293 K, after preliminary refinement of the C, S, N and O atoms of the *cc* conformer, difference electron-density maps for both compounds showed the H atoms and an additional peak appropriate to the alternative site for C(3) in the *cb* conformer. The H atoms and the additional C atom were then incorporated in subsequent least-squares calculations with the sum of the occupations of the major and minor sites for C(3) constrained to unity. The appropriate constraint was applied to the site occupation of the H atoms at C(3). Towards the end of the calculations for compound (5), when the occupation parameter of C(3') had settled at *ca* 0.3, C(3') was assigned an anisotropic thermal parameter; this had no significant effect on the occupation parameter. An isotropic thermal parameter was retained throughout for C(3') in compound (6), where the occupation parameter was smaller, *ca* 0.2. At convergence in these least-squares calculations, $R = 0.045$ for (5), 0.061 for (6), with C(3) *cc* occupation of 0.691 (16) for compound (5) and 0.795 (17) for compound (6). In both cases, $w = 1/\sigma^2(|F_o|)$; final $\Delta\rho$ maximum 0.23, minimum $-0.28 \text{ e } \text{\AA}^{-3}$ for compound (5); final $\Delta\rho$ maximum 0.28, minimum $-0.30 \text{ e } \text{\AA}^{-3}$ for compound (6); $\Delta/\sigma < 0.5$. Equivalent least-squares calculations for (6) with $w = 1$ converged at $R = 0.061$, $wR = 0.054$, with no significant difference in results, *cf.* *cc* occupation of 0.815 (17). For consistency, only results from calculations with $w = 1/\sigma^2(|F_o|)$, which have a better theoretical basis, are reported here, though $w = 1$ gave lower values of wR .

At the lowest temperatures, 130 K for compound (5) and 145 K for compound (6), there was no electron-density peak at the alternative *cb* site for C(3) in any of the difference electron-density distributions and attempts to include a partial C atom at that site in least-squares calculations gave an occupation of *ca* 0.00. Subsequent least-squares calculations without C(3') converged at $R = 0.047$ for (5), 0.040 for (6); final $\Delta\rho$ maximum 0.46 (in vicinity of S), minimum $-0.21 \text{ e } \text{\AA}^{-3}$ for (5); final $\Delta\rho$ maximum 0.42 (in vicinity of S), minimum $-0.44 \text{ e } \text{\AA}^{-3}$ for (6); no significant electron density at site for C(3').

At the intermediate temperatures, electron-density peaks were found at the *cb* site for C(3) and occupation parameters for C(3) and C(3') were successfully refined in least-squares calculations. As before, the sum of the occupations of C(3) and C(3') was constrained to unity. At 230 K for (5), refinement converged at $R = 0.049$, final $\Delta\rho$ maximum 0.41, minimum $-0.54 \text{ e } \text{\AA}^{-3}$. At 250 K for (5), convergence at $R = 0.051$, final $\Delta\rho$ maximum 0.36, minimum $-0.18 \text{ e } \text{\AA}^{-3}$. At 220 K for (6), convergence at $R = 0.054$, final $\Delta\rho$ maximum 0.54, minimum $-0.33 \text{ e } \text{\AA}^{-3}$. At 250 K for (6), convergence at R

$= 0.061$, final $\Delta\rho$ maximum 0.62, minimum $-0.37 \text{ e } \text{\AA}^{-3}$. In all cases, at convergence $\Delta/\sigma < 0.5$. Isotropic thermal parameters were retained for C(3').

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculations were performed on a SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985). Molecular diagrams were drawn with *ORTEP* (Johnson, 1965).

Coordinates and molecular geometries for compound (5) at 130 K and compound (6) at 145 K are listed in Tables 3–6.* The molecular structure of (5) at 130 and 293 K is shown in Fig. 1 and the molecular structure of (6) at 145 and 293 K is shown in Fig. 2.

Discussion

At the lowest temperatures, the crystal structures of the *p*-toluenesulfonylhydrazone (5) and the *p*-methoxybenzenesulfonylhydrazone (6) are fully ordered and both molecules exhibit the twin-chair *cc* conformation which is accepted as the most stable conformation of bicyclo[3.3.1]nonan-9-one. At higher temperatures the crystal structures become disordered, with the population of the chair-boat *cb* conformation increasing as the temperature is raised; the *cc/cb* populations derived from the least-squares analyses are shown in Table 7. The changes in the occupations of the *cc* and *cb* sites as the temperature is altered establish that a dynamic *cc* \rightleftharpoons *cb* interconversion is occurring in the solids.

At each temperature selected for data collection, the cell dimensions and the intensities of standard reflections quickly became stable and when the temperature was changed and then returned to that chosen for data collection the cell dimensions and standard intensities returned to the values appropriate to that temperature. This is consistent with the *cc/cb* system reaching equilibrium quickly.

The occupations of the *cc* and *cb* sites yield equilibrium constants for the *cc* \rightleftharpoons *cb* process and knowledge of these constants at several temperatures allows values of ΔH° and ΔS° for the conformational interconversion to be calculated. The results are included in Table 7. The differences in enthalpy between the *cc* and *cb* conformations, *ca* 6 kJ mol^{-1} for the *p*-toluenesulfonyl derivative (5) and

* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom coordinates and H-atom bond lengths and angles at 130, 145 and 293 K, and results at other temperatures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53271 (209 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for compound (5) at 130 K

	$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$.			U_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
S	0.22377 (8)	0.20330 (5)	0.48861 (4)	0.020
O(1)	0.4175 (2)	0.2994 (2)	0.5073 (1)	0.023
O(2)	0.1732 (3)	0.1710 (2)	0.5981 (1)	0.025
N(1)	0.2212 (3)	0.0473 (2)	0.2743 (2)	0.021
N(2)	0.1858 (3)	0.0468 (2)	0.3931 (2)	0.021
C(1)	0.2380 (4)	-0.0809 (2)	0.0740 (2)	0.028
C(2)	0.0438 (5)	-0.1767 (3)	-0.0387 (2)	0.036
C(3)	-0.0554 (4)	-0.3241 (2)	-0.0288 (2)	0.030
C(4)	-0.0645 (4)	-0.3158 (2)	0.1078 (2)	0.031
C(5)	0.1300 (4)	-0.2164 (2)	0.2182 (2)	0.023
C(6)	0.3045 (4)	-0.2635 (2)	0.2264 (2)	0.032
C(7)	0.3846 (5)	-0.2653 (2)	0.1135 (2)	0.032
C(8)	0.4098 (5)	-0.1311 (2)	0.0755 (2)	0.033
C(9)	0.1938 (3)	-0.0737 (2)	0.1992 (2)	0.020
C(10)	0.0513 (4)	0.2650 (2)	0.4147 (2)	0.021
C(11)	0.1153 (4)	0.3933 (2)	0.3900 (2)	0.022
C(12)	-0.0224 (4)	0.4432 (2)	0.3391 (2)	0.024
C(13)	-0.2238 (4)	0.3679 (2)	0.3107 (2)	0.027
C(14)	-0.2851 (4)	0.2394 (2)	0.3360 (2)	0.026
C(15)	-0.1490 (4)	0.1887 (2)	0.3877 (2)	0.026
C(16)	-0.3758 (5)	0.4212 (3)	0.2561 (2)	0.036

Table 5. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for compound (6) at 145 K

	$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}$.			U_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
S	0.74342 (7)	0.19643 (4)	0.50939 (3)	0.021
O(1)	0.6559 (2)	0.1572 (1)	0.6002 (1)	0.027
O(2)	0.9398 (2)	0.2902 (1)	0.5428 (1)	0.028
O(3)	0.2630 (3)	0.4566 (1)	0.2644 (1)	0.034
N(1)	0.7301 (3)	0.0374 (2)	0.4096 (1)	0.023
N(2)	0.8049 (3)	0.0484 (2)	0.3099 (1)	0.022
C(1)	0.8561 (3)	-0.0646 (2)	0.1134 (2)	0.024
C(2)	0.6890 (4)	-0.1156 (2)	-0.0001 (2)	0.033
C(3)	0.5285 (4)	-0.2582 (2)	-0.0231 (2)	0.035
C(4)	0.4735 (4)	-0.2699 (2)	0.0935 (2)	0.032
C(5)	0.6503 (3)	-0.2244 (2)	0.2006 (2)	0.024
C(6)	0.7829 (4)	-0.3229 (2)	0.1815 (2)	0.030
C(7)	0.9050 (4)	-0.3109 (2)	0.0891 (2)	0.029
C(8)	0.9989 (3)	-0.1527 (2)	0.1030 (2)	0.026
C(9)	0.7701 (3)	-0.0714 (2)	0.2199 (2)	0.023
C(10)	0.5943 (3)	0.2721 (2)	0.4374 (1)	0.023
C(11)	0.3938 (3)	0.2083 (2)	0.4035 (2)	0.025
C(12)	0.2757 (3)	0.2678 (2)	0.3462 (2)	0.025
C(13)	0.3651 (3)	0.3908 (2)	0.3220 (2)	0.026
C(14)	0.5649 (3)	0.4552 (2)	0.3567 (2)	0.027
C(15)	0.6812 (4)	0.3967 (2)	0.4153 (2)	0.024
C(16)	0.0564 (4)	0.4035 (2)	0.2360 (2)	0.035

Table 4. Interatomic distances (\AA) and angles ($^\circ$) for compound (5)

S—O(1)	1.421 (2)	S—O(2)	1.447 (2)
S—N(2)	1.636 (2)	S—C(10)	1.759 (3)
N(1)—N(2)	1.418 (3)	N(1)—C(9)	1.276 (3)
C(1)—C(2)	1.546 (4)	C(1)—C(8)	1.542 (5)
C(1)—C(9)	1.507 (4)	C(2)—C(3)	1.534 (4)
C(3)—C(4)	1.533 (4)	C(4)—C(5)	1.542 (4)
C(5)—C(6)	1.536 (5)	C(5)—C(9)	1.504 (3)
C(6)—C(7)	1.521 (4)	C(7)—C(8)	1.533 (4)
C(10)—C(11)	1.396 (3)	C(10)—C(15)	1.386 (4)
C(11)—C(12)	1.377 (4)	C(12)—C(13)	1.390 (4)
C(13)—C(14)	1.400 (4)	C(13)—C(16)	1.500 (4)
C(14)—C(15)	1.376 (4)		
O(1)—S—O(2)	119.7 (1)	O(1)—S—N(2)	108.9 (2)
O(1)—S—C(10)	108.7 (1)	O(2)—S—N(2)	102.4 (1)
O(2)—S—C(10)	107.6 (2)	N(2)—S—C(10)	109.2 (1)
N(2)—N(1)—C(9)	115.0 (2)	S—N(2)—N(1)	114.3 (2)
C(2)—C(1)—C(8)	114.5 (2)	C(2)—C(1)—C(9)	107.9 (3)
C(8)—C(1)—C(9)	109.3 (2)	C(1)—C(2)—C(3)	113.5 (2)
C(2)—C(1)—C(4)	112.1 (2)	C(3)—C(4)—C(5)	114.7 (3)
C(4)—C(5)—C(6)	116.0 (2)	C(4)—C(5)—C(9)	107.7 (2)
C(6)—C(5)—C(9)	107.2 (3)	C(5)—C(6)—C(7)	115.4 (3)
C(6)—C(7)—C(8)	112.3 (3)	C(1)—C(8)—C(7)	114.7 (3)
N(1)—C(9)—C(1)	118.2 (2)	N(1)—C(9)—C(5)	129.6 (2)
C(1)—C(9)—C(5)	112.2 (2)	S—C(10)—C(11)	120.5 (2)
S—C(10)—C(15)	119.2 (2)	C(11)—C(10)—C(15)	120.3 (3)
C(10)—C(11)—C(12)	119.3 (3)	C(11)—C(12)—C(13)	121.3 (2)
C(12)—C(13)—C(14)	118.5 (3)	C(12)—C(13)—C(16)	122.0 (3)
C(14)—C(13)—C(16)	119.4 (3)	C(13)—C(14)—C(15)	120.8 (3)
C(10)—C(15)—C(14)	119.8 (3)		

Table 6. Interatomic distances (\AA) and angles ($^\circ$) for compound (6)

S—O(1)	1.442 (2)	S—O(2)	1.422 (2)
S—N(1)	1.648 (2)	S—C(10)	1.759 (2)
O(3)—C(13)	1.370 (3)	O(3)—C(16)	1.414 (4)
N(1)—N(2)	1.401 (3)	N(2)—C(9)	1.282 (3)
C(1)—C(2)	1.538 (3)	C(1)—C(8)	1.529 (4)
C(1)—C(9)	1.507 (3)	C(2)—C(3)	1.531 (4)
C(3)—C(4)	1.534 (4)	C(4)—C(5)	1.540 (3)
C(5)—C(6)	1.548 (4)	C(5)—C(9)	1.506 (3)
C(6)—C(7)	1.525 (4)	C(7)—C(8)	1.527 (3)
C(10)—C(11)	1.380 (4)	C(10)—C(15)	1.391 (3)
C(11)—C(12)	1.391 (3)	C(12)—C(13)	1.395 (3)
C(13)—C(14)	1.376 (4)	C(14)—C(15)	1.384 (3)
O(1)—S—O(2)	119.8 (1)	O(1)—S—N(1)	103.2 (1)
O(1)—S—C(10)	108.9 (1)	O(2)—S—N(1)	108.4 (1)
O(2)—S—C(10)	108.2 (1)	N(1)—S—C(10)	107.8 (1)
C(13)—O(3)—C(16)	118.3 (2)	S—N(1)—N(2)	113.4 (2)
N(1)—N(2)—C(9)	116.4 (2)	C(2)—C(1)—C(8)	115.2 (2)
C(2)—C(1)—C(9)	109.0 (2)	C(8)—C(1)—C(9)	107.8 (2)
C(1)—C(2)—C(3)	115.4 (2)	C(2)—C(3)—C(4)	113.0 (2)
C(3)—C(4)—C(5)	114.1 (2)	C(4)—C(5)—C(6)	115.0 (2)
C(4)—C(5)—C(9)	106.7 (2)	C(6)—C(5)—C(9)	108.8 (2)
C(5)—C(6)—C(7)	115.5 (2)	C(6)—C(7)—C(8)	112.2 (2)
C(1)—C(8)—C(7)	113.4 (2)	N(2)—C(9)—C(1)	117.9 (2)
N(2)—C(9)—C(5)	129.9 (2)	C(1)—C(9)—C(5)	112.2 (2)
S—C(10)—C(11)	120.3 (2)	S—C(10)—C(15)	119.1 (2)
C(11)—C(10)—C(15)	120.5 (2)	C(10)—C(11)—C(12)	120.4 (2)
C(11)—C(12)—C(13)	118.5 (3)	O(3)—C(13)—C(12)	123.3 (3)
O(3)—C(13)—C(14)	115.6 (2)	C(12)—C(13)—C(14)	121.2 (2)
C(13)—C(14)—C(15)	120.0 (2)	C(10)—C(15)—C(14)	119.4 (3)

ca 12 kJ mol⁻¹ for the *p*-methoxybenzenesulfonyl derivative (6), are not far from the estimate of 4–7 kJ mol⁻¹ for the difference between the *cc* and *cb* conformations of bicyclo[3.3.1]nonan-9-one in the gas and liquid phases and it appears that movement of C(3) is not severely hindered by crystal packing forces. The crystal environment is of much greater importance for nitrogen inversion in 1,3,5-tribenzyl-

1,3,5-triazacyclohexane since the axial/equatorial enthalpy differences for the solid are 36–54 kJ mol⁻¹ (Sim, 1987), whereas the axial/equatorial enthalpy differences at the nitrogen atoms of *N*-methylpiperidine, *N,N'*-dimethylpiperazine, *etc.* in the liquid phase are *ca* 11–12 kJ mol⁻¹ (Riddell, 1980).

In the crystal structures of both (5) and (6), only one of the six-membered rings undergoes the chair \rightleftharpoons

boat interconversion and this presumably reflects the different crystal environments of C(3) and C(7). During the $cc \rightleftharpoons cb$ interconversion the methylene C(3) atom jumps *ca* 1.0 Å. For comparison, the methylene carbon atoms in the axial \rightleftharpoons equatorial interchange in 1,3,5-tribenzyl-1,3,5-triazacyclohexane move *ca* 1.4 Å (Sim, 1987).

The molecular geometries of compounds (5) at 130 K and (6) at 145 K are very similar. The arrangement of the sulfonyl and bicyclononane groups about the N—N bond is *trans*, with C(9)—N—N—S torsion angles of 179.4 (3)° in (5) and -168.9 (3)° in (6). The steric interaction of the

NH group with the C(5) region of the bicyclononane is alleviated by the angle C(5)—C(9)—N, 129.6 (2)° in (5) and 129.9 (2)° in (6), being substantially larger than the angle C(1)—C(9)—N, 118.2 (2)° in (5) and 117.9 (2)° in (6). The C(3)⋯C(7) separation is 3.124 (5) Å in (5) and 3.127 (5) Å in (6), very close to the separations in other bicyclononane derivatives, *e.g.* 3.134 (3) Å in 9-cyclohexylbicyclo[3.3.1]nonan-9-ol (Sim, 1983) and 3.128 (2) Å in 2,6-dinitrato-9-thiabicyclo[3.3.1]nonane-9,9-dioxide (McCabe & Sim, 1982).

The use of X-ray structural analysis at several temperatures has established a number of examples of conformational processes in the solid state: nitrogen inversion and axial \rightleftharpoons equatorial interchange in six-membered heterocycles (Sim, 1987), chair \rightleftharpoons boat interconversion of six-membered rings (this work), and ring-segment rotation in eleven-membered rings (G. A. Sim, unpublished results).

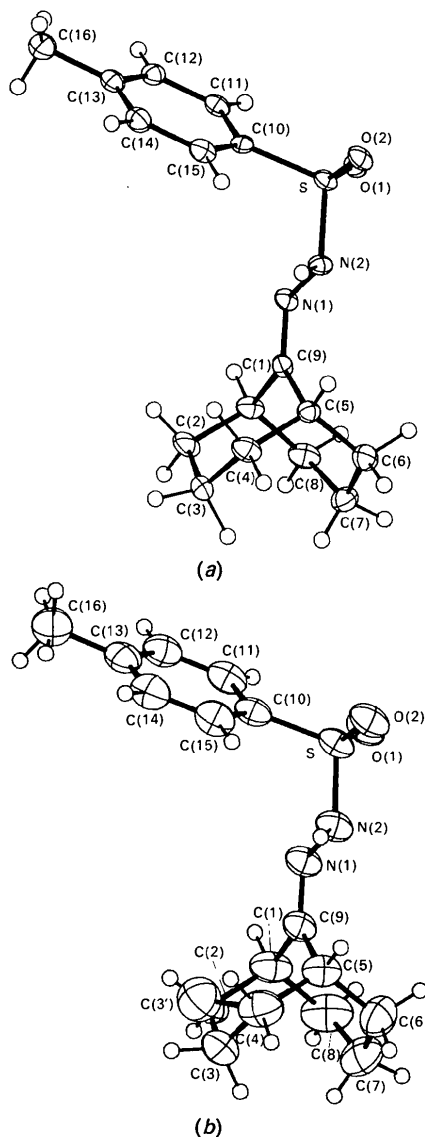


Fig. 1. The molecular structure and atomic numbering of compound (5) at (a) 130 K, (b) 293 K. The thermal ellipsoids are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å.

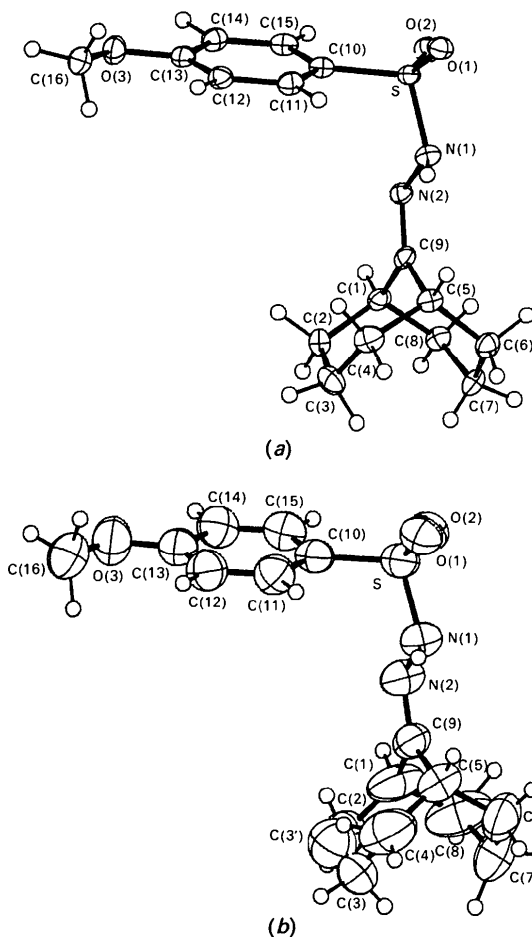


Fig. 2. The molecular structure and atomic numbering of compound (6) at (a) 145 K, (b) 293 K. The thermal ellipsoids are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å.

Table 7. Populations of *cc* and *cb* conformations, equilibrium constants, and thermodynamic parameters for the *cc*⇌*cb* interconversion in derivatives of bicyclo[3.3.1]nonan-9-one

<i>p</i> -Toluenesulfonylhydrazone (5)				
	130 K	230 K	250 K	293 K
<i>cc</i> population	1.000	0.819 (9)	0.769 (10)	0.691 (16)
<i>cb</i> population	0.000	0.181 (9)	0.231 (10)	0.309 (16)
<i>K</i>		0.221 (14)	0.300 (17)	0.447 (34)
ΔG° (kJ mol ⁻¹)		2.89 (18)	2.50 (14)	1.96 (15)
ΔH° (kJ mol ⁻¹)			6 (1)	
ΔS° (J K ⁻¹ mol ⁻¹)			15 (2)	

<i>p</i> -Methoxybenzenesulfonylhydrazone (6)				
	145 K	220 K	250 K	293 K
<i>cc</i> population	1.000	0.958 (8)	0.915 (14)	0.795 (17)
<i>cb</i> population	0.000	0.052 (8)	0.085 (14)	0.205 (17)
<i>K</i>		0.054 (9)	0.093 (17)	0.258 (27)
ΔG° (kJ mol ⁻¹)		5.34 (90)	4.93 (90)	3.30 (35)
ΔH° (kJ mol ⁻¹)			12 (2)	
ΔS° (J K ⁻¹ mol ⁻¹)			30 (4)	

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