# Conformational Analysis. Part 17.[1] An NMR and Theoretical Investigation of the Conformation of Bicyclo[5.2.1]decane-2,6-dione

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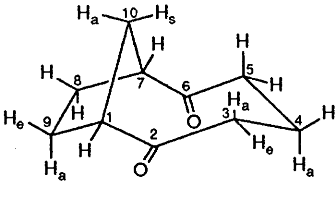
The conformation of bicyclo[5.2.1]decane-2,6-dione in solution has been investigated by molecular modelling and the lanthanide-induced shift (LIS) technique. Of the five possible conformers two were eliminated due to their large calculated steric energy and a third 'twist' conformer due to the observed symmetry in the $^{13}$C NMR and the $^{1}$H NMR spectra. The remaining *exo* and *endo* conformers were calculated as having an energy difference of 1.5 kcal mol$^{-1}$†. However, MNDO calculated the *endo* form as the more stable in contrast to MM2 and COSMIC which gave the reverse order. The LIS investigation was in agreement with a lanthanide monodentate complex bound to the *exo* form only confirming the MM2 and COSMIC calculations.

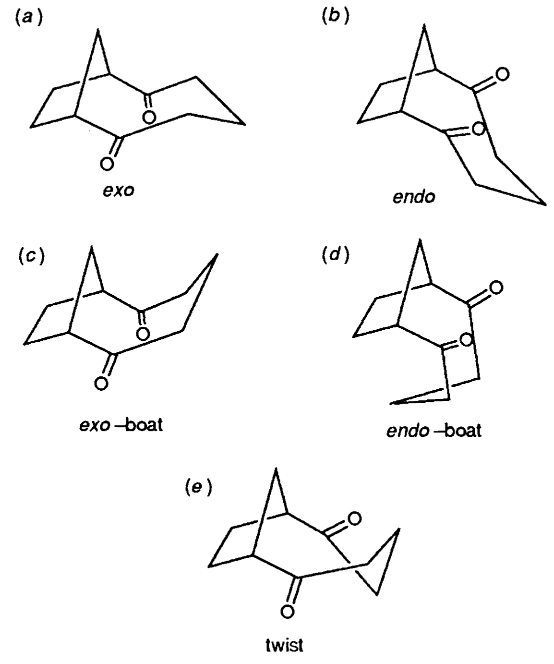
In previous work, the preparation and spectroscopic data of bicyclo[5.2.1]decane-2,6-dione **1** were reported.[2] Analysis of the $^{1}$H NMR spectrum gave the chemical shifts and vicinal couplings for the C-3 to C-5 part of the molecule (Fig. 1), from which it was clear that this part of the molecule existed in a cyclohexane type staggered conformation. However, the conformation of the molecule could not be obtained from the NMR data, and it was thus felt of interest to attempt this by the lanthanide-induced shift (LIS) technique. Abraham *et al.* have, in a series of publications[3–12] demonstrated the application of the LIS technique to the conformational analysis of a variety of molecules, including several cyclic ketones, using the LIRAS3 program. These investigations have evolved a procedure in which the LIS experiment is used to determine a particular aspect of a molecular geometry. In the present investigation a number of possible molecular geometries were obtained by theoretical calculations [Fig. 2(*a*)–(*e*)] and the LIS technique used to distinguish between the stable conformers.

The initial investigation into the possible geometry of bicyclo[5.2.1]decane-2,6-dione (**1**) was carried out using two different theoretical methods: semi-empirical *via* the computer program MNDO[13] and Allinger's MM2 force field,[14] the latter being used in conjunction with the molecular modelling package PCMODEL.[15,16] The initial geometries were generated by assuming a norbornane geometry to which was added a five membered ring, with a flip angle of *ca.* +40 °C, and the two carbonyl functions. The molecules were then fully optimised using the PCMODEL force field with all parameters relaxed. These optimised geometries were then in turn used as the initial starting point for a full optimisation by MNDO. The MNDO calculated heat of formation together with the total energies from PCMODEL, for each optimised geometry, are shown in Table 1. Examination of these values indicates that both of the boat forms are clearly unfavourable compared to the chair forms, and these will not be considered further. Both MNDO and MM2 calculate the chair forms as being more favourable, but differ on which of these forms is the most stable. Although both calculate a similar Δ*E*, *ca.* 2.5 kcal mol$^{-1}$, MNDO favours the *endo*-chair form whereas MM2 favours the *exo*-chair form. In the hope of clarifying which of the two forms is the more favoured, a further optimisation was carried out using a more recent force field molecular modelling program COSMIC.[17] This force field calculates that the optimised *exo* form is more stable than the *endo* form by 1.2 kcal mol$^{-1}$. Examination of the optimised geometries, using all three methods reveals that the calculated geometries by MM2, COSMIC and MNDO are very similar, for both the *exo* and *endo* forms, despite the difference in the calculated energies.



**1**

**Fig. 1** Numbering in bicyclo[5.2.1]decane-2,6-dione



*exo*

*endo*

*exo*-boat

*endo*-boat

twist

**Fig. 2** (*a*)–(*e*) Proposed possible conformations of bicyclo[5.2.1]decane-2,6-dione

In the calculated geometries of the two chair forms [Fig 2(*a*)

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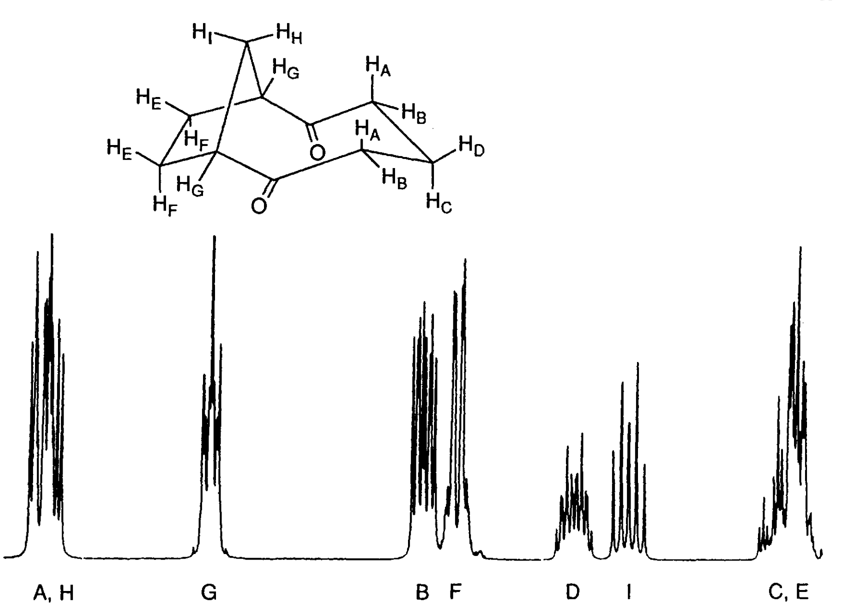
† 1 cal = 4.18 J.

(a) Calculated



(b) Observed

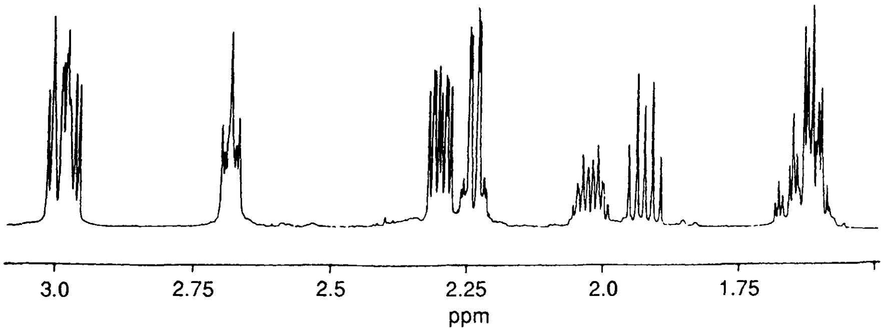


**Fig. 3** (*a*) Simulated and (*b*) observed 500 MHz $^1$H NMR spectra of bicyclo[5.2.1]decane-2,6-dione

**Table 1** Calculated energies and heats of formation ($H^f$/kcal mol$^{-1}$) for the proposed geometries of **1**[a]

| | Conformation | | | | |
|---|---|---|---|---|---|
| | (*a*) | (*b*) | (*c*) | (*d*) | (*e*) |
| MM2 Total energy | 25.89 | 28.28 | 31.21 | 32.61 | |
| MNDO $H^f$ | −79.45 | −82.03 | −73.29 | −72.40 | −80.29 |
| COSMIC total energy | 16.06 | 17.30 | | | |
| MNDO[b] $H^f$ | −78.99 | −81.57 | | | |

[a] See Fig. 2 for conformations (*a*)–(*e*). [b] Dihedral angle C(1)–C(9)–C(8)–C(7) = 0.0° inducing symmetry throughout the molecule

**Table 2** Observed $^1$H and $^{13}$C chemical shifts for bicyclo[5.2.1]decane-2,6-dione

| $^1$H[a] | | $^{13}$C[b] | |
|---|---|---|---|
| 1-H | 2.678 | C-1<br>C-7 | 51.34 |
| 3-H$_a$ | 2.977 | | |
| 3-H$_e$ | 2.291 | C-2<br>C-6 | 213.98 |
| 4-H$_a$ | 1.629 | | |
| 4-H$_e$ | 2.015 | C-3<br>C-5 | 39.10 |
| 9-H$_a$ | 2.229 | | |
| 9-H$_e$ | 1.607 | C-4 | 24.73 |
| 10-H$_s$ | 2.982 | C-8<br>C-9 | 23.57 |
| 10-H$_a$ | 1.916 | | |
| | | C-10 | 30.94 |

[a] All shifts relative to CHCl$_3$ (7.260 ppm). [b] All shifts relative to TMS (0.0 ppm).

and (*b*)] the dihedral angle [C(1)–C(9)–C(8)–C(7)] is not zero but *ca.* 10°. A symmetrical geometry, with a plane of symmetry through C-10 and C-4 was calculated by optimising the geometry with the dihedral angle C(1)–C(9)–C(8)–C(7) fixed at 0.0°, in both *endo* and *exo* forms. These optimised geometries were found by MNDO to have very similar heats of formation to those calculated for the fully optimised molecules (Table 1). The fixing of this dihedral inflicts symmetry throughout the molecule, without significant energy change. Consequently it was decided that these symmetrical geometries were ideal for use as the primary geometry in the LIS calculations.

It was noted previously that the proton–proton couplings in the C-3 to C-5 fragment were characteristic of a cyclohexane type staggered conformation. Thus this definitely excludes both the twist conformation and a conformation rapidly interconverting between two twist forms.

*NMR Analysis*.—The $^1$H NMR spectrum of **1** even at high field strengths is not first order (Fig. 3). The preliminary assignment of this spectrum was carried out using the double-resonance technique.[2] This method, as well as provisionally assigning the spectra, was also able to reveal some (but not all) of the couplings present in this molecule. A $^{13}$C DEPT NMR spectrum was also recorded,[2] but not fully assigned. The observed $^{13}$C spectrum revealed only six resonances, indicating complete symmetry throughout the molecule. The six observed resonances have been partly assigned: C-2, C-6 213.98 ppm; C-1, C-7 (tertiary) 51.34; C-3, C-5 39.10 (deshielded due to adjacent carbonyl groups); and C-10 30.94 (*cf.* bicyclo[2.2.1]heptane[18]). The remaining two resonances due to C-9 and C-8, and C-4 have not been assigned. In order to confirm

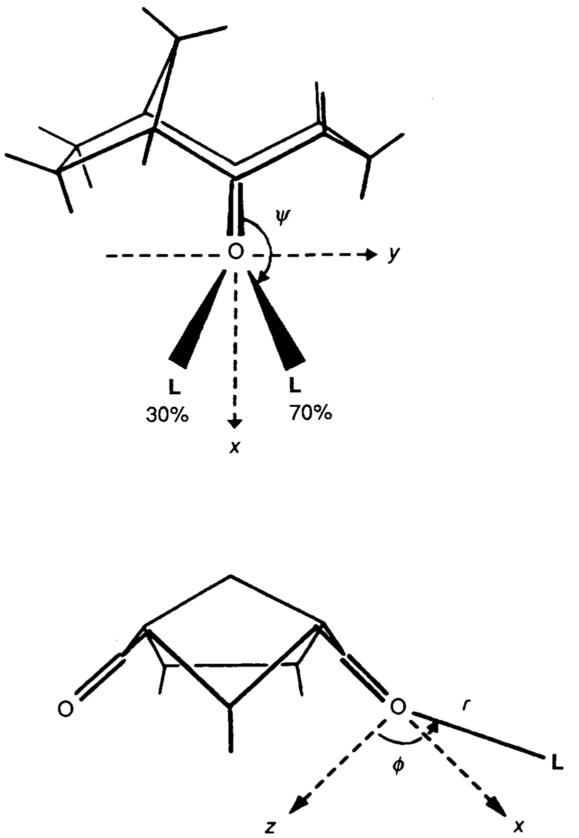


**Fig. 4** LIRAS3-calculated lanthanide complexation geometry for the *exo*-chair geometry

**Table 3** Observed coupling constants for bicyclo[5.2.1]decane-2,6-dione

| Proton coupling | Observed $J$/Hz |
|---|---|
| $3_a,3_e$ | 11.59 |
| $3_a,4_e$ | 3.86 |
| $3_a,4_a$ | 13.10 |
| $3_e,4_e$ | 5.27 |
| $3_e,4_e$ | 3.54 |
| $4_a,4_e$ | −13.29 |
| $1,10_a$ | 7.43 |
| $1,10_s$ | 0.2[a] |
| $1,9_e$ | 7.3[a] |
| $1,9_a$ | 0.5[a] |
| $9_e,9_a$ | −12.5[a] |
| $9_e,8_e$ | 10.0[a] |
| $9_e,8_a$ | 5.0[a] |
| $9_a,8_a$ | 8.0[a] |
| $9_a,10_s$ | 1.8 |
| $10_a,10_s$ | −14.05 |

[a] Optimised by PANIC simulation

the $^1$H NMR assignments, fully assign the $^{13}$C NMR spectra and also obtain a more complete picture of the coupling pathways in the molecule, both spectra were re-examined with the aid of $^1$H/$^1$H and a $^{13}$C/$^1$H correlated 2D spectra. Inspection of these gives the complete assignment of both the $^1$H and $^{13}$C spectra (Table 2), that of the $^1$H spectrum confirming the previous provisional assignment.[2]

The observed couplings between the bridgehead protons and the C-10 protons ($J_{1,10_a}$ 7.4 Hz, $J_{1,10_s} > 1.0$ Hz) contrasts strongly with those observed in the similar bicyclo[2.2.1]heptane system, norcamphor,[19] where the equivalent bridgehead proton has two small couplings to $10_a$ and $10_s$ protons (1.19 and 1.64 Hz respectively) clearly indicating a significant difference in the bridgehead geometries between the two molecules.

Using the optimised geometries obtained by MM2, the anisotropic effect of the carbonyl function on the β protons can be calculated using the method of prediction suggested by Pople.[20] The estimates obtained for *endo* and *exo* forms (*ca.* 3-H$_e$ −0.6, 3-H$_a$ −0.1 and 3-H$_a$ −0.1, 3-H$_e$ −0.45) indicate that the equatorial proton is deshielded to a greater extent (*ca.* 0.5 ppm) in both the *exo* and *endo* forms than is the axial proton. This is in agreement with a recent analysis of substituent effects in the cyclohexanoid system,[21] where it was found that the β equatorial proton is deshielded by 0.98 ppm compared to 0.80 ppm for the β axial proton. Furthermore, in cyclohexane derivatives equatorial protons are found to be downfield from the corresponding axial protons by *ca.* 0.5–1.0 ppm. Combining these two effects one could clearly expect the β equatorial proton to be downfield from the axial proton, however, in the observed spectra the equatorial proton resonates *ca.* 0.3 ppm upfield of the axial proton. This disagreement may be due to the effect of the adjacent norbornane group.

Having been assigned, the $^1$H NMR spectra can be fully analysed. The spectra may be subdivided into two separate parts, an eight-spin spectrum (AA'BB'CC'DE) of the bicycloheptane part of the molecule and a six-spin (AA'BB'CD) spectrum of the cyclohexane like part of the molecule. Analysis of these spin systems using the PANIC program, gave the couplings shown in Table 3 and the calculated spectra of Fig. 3, shown with the observed spectrum.

The couplings in the C-3,C-4,C-5 fragment are closely similar to those of cyclohexane,[22] which suggests an angle of flip ≈60°, for the uncomplexed molecule in solution. The observed couplings, as well as inferring the geometry of this part of the molecule, are not consistent (like the $^{13}$C NMR spectrum) with the proposed 'twist' molecule. In the 'twist' geometry the coupling between the 3-H$_a$ and 4-H protons would have to be an average of *ca.* 7 Hz, not the observed large *trans* and small *cis* values observed ($J_{3_a,4_a}$ 13.10 Hz, $J_{3_a,4_e}$ 3.86 Hz). The coupling constants were observed over a range of temperatures (−99 to −45 °C) and found to be invariant, confirming a rigid geometry in the cyclohexane part.

*LIS Analysis.*—The observed proton and carbon lanthanide-induced chemical shifts ($\Delta M$) are shown in Table 4. These observed shifts were compared with those calculated, using the LIRAS3 program, for various molecular and lanthanide binding geometries. Calculated values are given in Table 5.

In contrast to earlier LIS investigations in the series, where the molecules concerned were monofunctional, this diketone can adopt several additional lanthanide complexation models, these being a chelate complex, where a single lanthanide binds simultaneously to both carbonyl functions and also a binuclear complex ($L_2S$) where two molecules of lanthanide shift reagent bind to the substrate, one to each carbonyl. In order to calculate which is the preferred diketone geometry, one needs to calculate the LIS values for the above complexation models and also the simple monodentate complex (LS) where one lanthanide binds to just one carbonyl.

The first complexation model examined was that of the simple monodentate case. The diketone geometries used were those obtained by MNDO, where symmetry had been imposed. The use of the symmetrical molecular geometries, for the *endo*-chair and *exo*-chair diketones, significantly simplifies the LIRAS3 calculations, since now both of the carbonyl groups are identical. The LIRAS3 program can be used for unsymmetrical molecules, the calculated LIS values simply being an average of those calculated for complexation to each individual carbonyl. The LIS calculation on the symmetrical geometries, although

**Table 4** Observed $^{13}C$ and $^{1}H$ shifts ($\delta$), intercept values ($\delta_{INT}$) and LIS values ($\Delta M$) (all in ppm)

| | C-1,C-7 | C-2,C-6 | C-3,C-5 | C-4 | C-9,C-8 | C-10 | 1-H | 3-$H_a$ | 3-$H_e$ | 4-$H_a$ | 4-$H_e$ | 9-$H_a$ | 9-$H_e$ | 10-$H_s$ | 10-$H_a$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\delta^a$ | 51.34 | 213.98 | 39.10 | 24.73 | 23.57 | 30.94 | 2.68 | 2.98 | 2.29 | 1.63 | 2.01 | 2.23 | 1.61 | 2.98 | 1.92 |
| $\delta_{INT}$ | 51.49 | 214.07 | 39.23 | 24.86 | 23.75 | 31.08 | 2.69 | 2.99 | 2.29 | 1.62 | 2.03 | 2.23 | 1.61 | 2.99 | 1.92 |
| $\Delta M^b$ | 37.11 | 73.27 | 37.74 | 30.38 | 29.10 | 26.29 | 24.57 | 22.30 | 26.85 | 29.86 | 15.12 | 28.52 | 14.07 | 22.30 | 15.61 |
| Correlation coefficient | 0.991 | 0.999 | 0.993 | 0.989 | 0.980 | 0.985 | 0.998 | 0.997 | 0.999 | 0.998 | 0.998 | 0.999 | 0.997 | 0.997 | 0.997 |

[a] $[S]_0 \approx 0.9$ mol $dm^{-3}$ in $CDCl_3$. All shifts referenced to TMS. [b] Five additions of $Yb(fod)_3$, $\rho = 0.0, 0.31, 0.94, 2.45, 3.20$ and $4.40 \times 10^{-2}$.

**Table 5** Calculated lanthanide-induced shifts for bicyclo[5.2.1]decane-2,6-dione (*exo*-chair form)

| | Lanthanide induced shift (ppm) | | |
|---|---|---|---|
| | | Calculated | |
| Atom | Observed | *a* | *b* |
| C-1,C-7 | 37.1 | 37.1 | 37.5 |
| C-2,C-6 | 73.3 | 74.4 | 74.6 |
| C-3,C-5 | 37.7 | 36.3 | 37.0 |
| C-4 | 30.4 | 28.4 | 27.6 |
| C-9,C-8 | 29.1 | 27.1 | 27.4 |
| C-10 | 26.3 | 24.8 | 24.6 |
| 1-H | 24.6 | 26.1 | 25.4 |
| 3-$H_a$ | 22.3 | 22.7 | 23.1 |
| 3-$H_e$ | 26.9 | 28.0 | 29.8 |
| 4-$H_a$ | 29.9 | 30.7 | 27.2 |
| 4-$H_e$ | 15.1 | 15.6 | 15.9 |
| 9-$H_a$ | 28.5 | 29.4 | 30.1 |
| 9-$H_e$ | 14.1 | 14.8 | 14.2 |
| 10-$H_s$ | 22.3 | 21.1 | 20.8 |
| 10-$H_a$ | 15.6 | 15.7 | 15.0 |

[a] Lanthanide co-ordination geometry $r = 2.45$ Å, $\varphi = 115°$ and $\psi = 165°$ with *R*(cryst) = 3.651% (all shifts). [b] Dihedral angle C(2)–C(3)–C(4)–C(5) = 60°. Lanthanide co-ordination geometry $r = 2.40$ Å, $\varphi = 120°$ and $\psi = 175°$ with *R*(cryst) = 5.048% (all shifts).

less complex, is felt to be equally as good, since the small calculated energy difference between the unsymmetric and symmetric forms implies insignificant geometry differences.

In the case of this simple monodentate complex, an initial two site geometry was examined (Fig. 4), where the lanthanide shift reagent binds to two sets of lone pairs on the carbonyl, above or below the plane of the carbonyl bond ($\varphi$ being < or > 90°, respectively) with one side simply being a reflection of the other in the *xz* plane. The first diketone geometry considered was that of the *exo*-chair, favoured by the COSMIC and MMPMI, but not MNDO. The lanthanide complexation geometry was optimised by variation of $r$, $\psi$, $\varphi$ (2.00–3.00 Å, 0–180° and 0–180°, respectively) the best solution being obtained when $r = 2.45$ Å, $\varphi = 115°$ and $\psi = 165°$, with an *R*-factor of 3.651% (Fig. 4). The two lanthanide sites have identical geometries but do not have equal population, there being a large preference for the sterically less hindered (positive side) of the carbonyl. The calculated LIS values for this complexation geometry gave good overall agreement (Table 5). All the shifts are within acceptable error, and this gives a chemically reasonable solution which also reflects the different steric environment of the two sites.

The same procedure as above was carried out for the *endo*-chair diketone. In contrast to the case above, no acceptable solution could be obtained. The best solution obtained using all the shifts gave *R*(cryst.) = 12.71%, and complexation geometry $r = 2.45$ Å, $\varphi = 70°$, $\psi = 175°$ with 35% population in the $+y$ co-ordination site (Fig. 4). Upon removal of the C(2)/C(6) carbon LIS, still no acceptable solution could be obtained, in fact the latter solution was worse (the variables being fixed within the ranges previously mentioned).

Both geometries were then investigated assuming a chelate complexation geometry, where the lanthanide binds to both carbonyls simultaneously. Upon optimisation no solution could be obtained in the case of *endo* or *exo* forms, where the lanthanide adopts a geometry which would indicate a chelate complex. Hence, having examined both possible complexation modes, it is clear that the LIS data is consistent only with the *exo*-chair conformation in solution.

In order to attempt to refine the *exo*-chair geometry, having established it as the species present in solution, the geometry of this diketone when the dihedral angle [C(2)–C(3)–C(4)–C(5)] was at 60.0° was examined. As mentioned previously the proton–proton couplings implied that the cyclohexane part of the molecule had a dihedral angle [C(2)–C(3)–C(4)–C(5)] nearer 60.0° than the previously (MNDO) calculated value of 79.6°. Consequently the molecule was optimised with this dihedral fixed at 60.0°. The calculated geometry was slightly more unstable, $H^f = -77.19$ kcal mol$^{-1}$, the energy difference between the two *exo*-chair forms being 1.8 kcal mol$^{-1}$. Examination of the actual structure revealed, not unexpectedly, that the bicyclo part of the molecule remains virtually unchanged. Lanthanide shift analysis of this molecule, using all the shifts in calculation gave a poorer solution than previously, with *R*(cryst.) = 5.05% and complexation geometry parameters of $r = 2.40$ Å, $\varphi = 120°$, $\psi = 175°$, [65% population in one side ($+y$ site)]. This solution is just within the bounds of mathematical acceptability.[23] Thus, the LIS analysis is able to clearly distinguish which of the five possible conformers exist in solution, but the actual observed coupling constants are probably a more accurate indication of the exact *exo*-chair geometry than the LIS results.

## Experimental

A sample of bicyclo[5.2.1]decane-2,6-dione was obtained as a by-product of the oxidation of *endo*-tetrahydrodicyclopentadiene,[2] and was isolated and purified before use.

The $^{1}H$ and $^{13}C$ NMR spectra were obtained at 500.13 and 125.6 MHz, respectively, using a Bruker AM-500 spectrometer fitted with the Aspect 3000 microcomputer system. The solvent was $CDCl_3$ and spectra were recorded at room temperature. The $^{1}H$ NMR spectrum used for spectral assignments (0.1 mol dm$^{-3}$) was obtained from an FID recorded over 64 transients, of sweep width 4000 Hz (acquisition time of 1.98 s) in 16 K memory space. The FID was transformed into 64 K memory space, following the use of gaussian resolution enhancements (factors LB = −0.5, GB = 0.20), giving a digital resolution of 0.126 Hz per point. The 2D-COSY spectrum was acquired on a Bruker AM500 spectrometer using 2 K data points, a spectral sweep width of 904 Hz and a sine-bell squared multiplication to avoid truncation artifacts. 256 Experiments were recorded, each involving 32 transients with 2 dummy scans. The $^{1}H/^{13}C$-correlated 2D experiment was performed using the Bruker automated program XHCORR.Au. The spectrum was acquired with sweep widths of SW1($^{1}H$) = 450 Hz and SW($^{13}C$) = 4166

Hz and a size SI1 = 512W and SI = 4 K, respectively. A total of 232 experiments were recorded, each with 32 transients and 2 dummy scans. Proton decoupling was achieved using a decoupler power of 12 H and a 'sine bell squared' window function was used for the 2D Fourier transformation.

The LIS experiment was carried out using the incremental weighting method,[3-4] in which weighted amounts of shift reagent [Yb(fod)$_3$] were added directly to a known amount of substrate. The correlation coefficient was obtained from a plot of $\rho$ *vs.* observed shift for each atom, where $\rho$ = [L]/[S] (L = shift reagent, S = substrate) in the range 0.00–0.04. The linearity of the plots is substantially better for the protons than for the carbons. This slight deviation from linearity for the carbon shifts is emphasised by the difference between the calculated intercept values $\delta_{INT}$ (from the best straight line fit) and the observed carbon shifts at $\rho = 0$ (*i.e.*, no lanthanide shift reagent added). All the calculated $\delta_{INT}$ values are slightly larger than the observed shifts in contrast to normal errors in these experiments, where trace of impurity or water gives calculated $\delta_{INT}$ values smaller than the observed shifts. This anomalous behaviour was also seen previously in the LIS investigation of benzophenone,[4] where removal of the $\rho = 0$ point increased the linearity of the plot but had relatively little effect on the $\Delta M$ value. As a consequence of this calculation the inclusion of all the points, although giving slight deviation from linearity, can be justified. The observed shifts ($\delta$) and lanthanide induced shifts ($\Delta M$) for bicyclo[5.2.1]decane-2,6-dione, are shown in Table 4. The PANIC simulations were carried out using the PANIC software, on a Bruker Aspect 3000 computer.

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