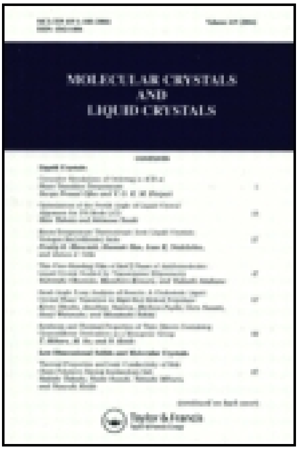

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

NMR Spin-Lattice Relaxation Time Determination of the Barriers to Ring Rotation in SOlid bid-Cyclopentadienyl Molybdenum Dichloride

Ian S. Butler [a], Paul J. Fitzpatrick [a], D. F.R. Gilson [a], Gerry Zomez [a] & Alan Shaver [a]

[a] Department of Chemistry, McGill University, 801 Sherbrooke Street, W., Montreal, H3A 2K6, Quebec, Canada

Version of record first published: 20 Apr 2011.

To cite this article: Ian S. Butler, Paul J. Fitzpatrick, D. F.R. Gilson, Gerry Zomez & Alan Shaver (1981): NMR Spin-Lattice Relaxation Time Determination of the Barriers to Ring Rotation in SOlid bid-Cyclopentadienyl Molybdenum Dichloride, Molecular Crystals and Liquid Crystals, 71:3-4, 213-218

To link to this article: http://dx.doi.org/10.1080/00268948108072322

Mol. Cryst. Liq. Cryst., 1981, Vol. 71, pp. 213–218
0026-8941/81/7104-0213/$06.50/0

NMR Spin-Lattice Relaxation Time Determination of the Barriers to Ring Rotation in Solid bis-Cyclopentadienyl Molybdenum Dichloride

IAN S. BUTLER, PAUL J. FITZPATRICK, D. F. R. GILSON†, GERRY GOMEZ AND ALAN SHAVER

Department of Chemistry, McGill University, 801 Sherbrooke Street, W., Montreal H3A 2K6 Quebec, Canada.

(*Received August 8, 1980; in final form December 23, 1980*)

The potential energy barriers to rotation of the cyclopentadienyl rings in bis-cyclopentadienyl molybdenum dichloride have been measured by spin-lattice relaxation time methods. The barrier depends upon the local environment of the ring and values of 12.76, 8.64, 8.64, and 1.47 kJ mol^{-1} were obtained for the four crystallographically unique cyclopentadienyl rings of the two molecules in the asymmetric unit.

INTRODUCTION

Although the "sandwich" structure of ferrocene was established nearly thirty years ago the crystal structure and molecular conformation are still in doubt. Originally the conformation was believed to be staggered since the iron atoms apparently occupied centres of inversion, but recent X-ray and neutron diffraction studies[1-3] have shown that the room temperature structure is disordered, and, as a result, the individual molecules need not possess the centres of symmetry required by the space group for an ordered phase. In the low temperature triclinic phase[3] the conformation is closer to eclipsed than staggered with a rotation of one ring with respect to the other of about 9°. Electron diffraction studies[4] of ferrocene in the vapour phase support an eclipsed structure with a barrier to rotation of less than 4 kJ mol^{-1}. In the solid

---

†To whom correspondence should be addressed.

state the barrier has been measured by spin-lattice relaxation time methods[5] as 8.33 kJ mol^{-1} in the low temperature phase and it is probably much lower in the high temperature monoclinic phase. Campbell *et al*[5] have calculated the intra- and inter-molecular contributions to the rotational barrier using the atom-atom potential method but based upon the earlier interpretation of the crystal structure.[6] However, their conclusions are still correct in that the intramolecular contribution to the barrier in the solid is small, if not zero. Thus the molecular conformation is determined by intermolecular interactions, i.e. packing forces.

In molecules of the "slipped sandwich" type such as bis-cyclopentadienyl metal dichloride complexes the internal barrier cannot be zero and the conformation will depend upon a balance between the intra- and inter-molecules contributions. An interesting situation arises in the isomorphous and isostructural compounds $(C_5H_5)_2MoCl_2$ and $(C_5H_5)_2NbCl_2$ where Prout and co-workers[7] have reported that of the two molecules in the asymmetric unit one is staggered and the other eclipsed. This implies that there should be at least two different barriers to rotation of the cyclopentadienyl rings in these crystals. We report here the results of a spin-lattice relaxation time investigation of the barriers in the molybdenum complex.

EXPERIMENTAL

Bis-cyclopentadienyl molybdenum dichloride was prepared by the method of Cooper and Green.[8] T_1 measurements were made using a Spin-Lock CP2 pulsed nmr spectrometer operating at 33 MHz. A 180°–τ–90° pulse sequence was used and the free induction decays captured with a Biomation 805 transient recorder and then plotted on a strip chart recorder. The sample temperature was varied using a gas flow system and measured with a copper-constantan thermocouple inserted next to the sample.

RESULTS AND DISCUSSION

The observed spin-lattice relaxation times are plotted versus reciprocal temperature in Figure 1. For a single process the relaxation rate is given by Eq. (1).

$$(T_1)^{-1} = \frac{2}{3}\cdot C\cdot\left[\frac{\tau}{1+\omega_0^2\tau^2} + \frac{4\tau}{1+4\omega_0^2\tau^2}\right] \tag{1}$$

where $\tau = \tau_0 \exp(E/RT)$ is a correlation time for the motion and C is related to the change in second moment of the resonance line shape. This expression

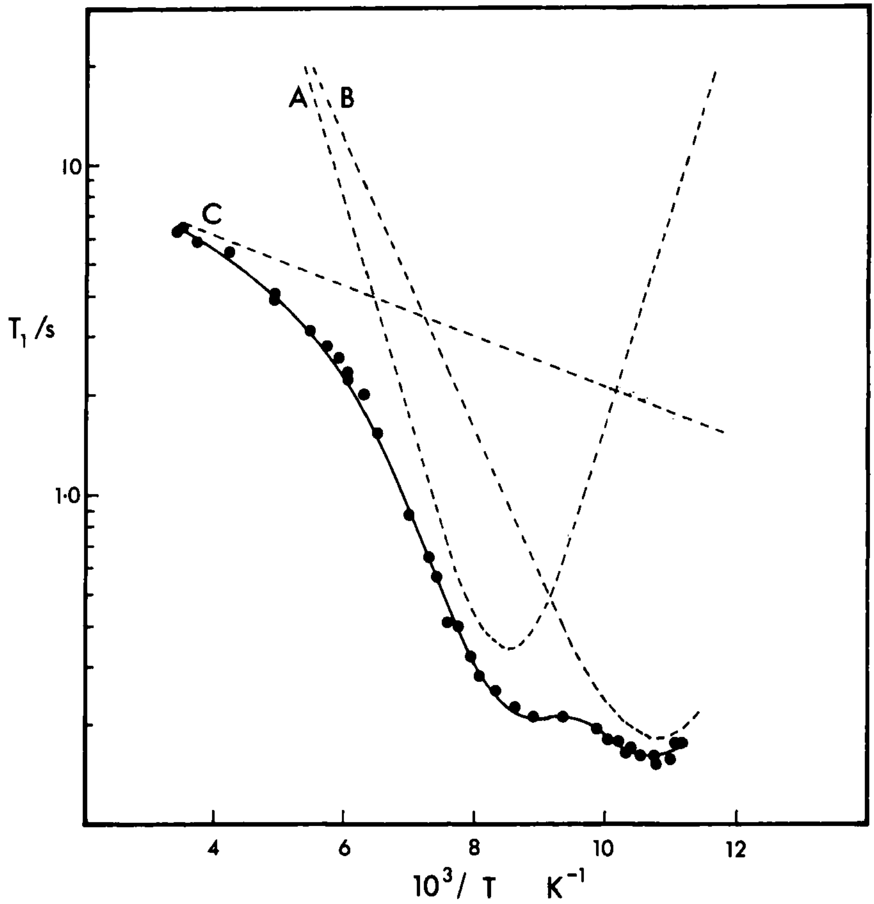

FIGURE 1 Spin-lattice relaxation time, T_1, versus reciprocal temperature. The solid curve is the calculated fit and the dotted curves the individual contributions.

for T_1 exhibits a minimum when $\omega_0\tau \sim 0.62$ and it is apparent from Figure 1 that the observed minimum can only be explained by multiple contributions and, furthermore, from the change in slope at about 200K we conclude that at least three T_1 processes must be involved. If rapid equilibration between spins occurs so that at any temperature a single relaxation time describes the system, then

$(T_1^{\text{exp}})^{-1} = \sum_i p_i / T_1^i$, where p_i is the relative fraction of protons (or, alternatively, of the number of cyclopentadienyl rings) involved in each motion. An initial non-linear least squares computer fit to the experimental T_1 data showed that for one process a very low barrier was involved and therefore no

TABLE I

	τ_0 s	C rad s^{-2}	E kJ mol^{-1}
A	$6.26 \pm .72 \times 10^{-15}$	$6.36 \pm .46 \times 10^{8}$	12.76 ± 1.11
B	$4.04 \pm .23 \times 10^{-14}$	$1.20 \pm .22 \times 10^{9}$	8.64 ± 4.2
C	—[a]	—[a]	$1.47 \pm .64$

a) $C\tau_0 = 8.07 \pm 3.8 \times 10^{-2}$ rad s^{-1}

T_1 minimum occurred within the temperature range of these experiments. The "high temperature" limit of Eq. (1) was used in this case, since $\omega_0\tau \ll 1$, Eq. (2)

$$(T_1)^{-1} = \frac{10}{3} C \tau_0 \exp (E/RT) \tag{2}$$

and the two terms C and τ_0 cannot be separated. An acceptable fit to the experimental data was obtained with three processes, Table I and Figure 1. In principle a fit with four T_1 curves could be made, with eleven adjustable parameters, but would not improve upon the present results. The values of E and $C\tau_0$ for the low energy barrier are not particularly well defined since only the high temperature points are affected significantly by this contribution. For the remaining contributions the values of C were in the approximate ratio of two to one and since this parameter is related to the change of the second moment† due to ring reorientation there must be two cyclopentadienyl rings with approximately the same barrier to rotation, 8.64 kJ mol^{-1}, and giving rise to the T_1 curve with the lower T_1 minimum. Thus there are two reorientational barriers of about the same value, plus single processes with a higher and a much lower barrier respectively, accounting for the four cyclopentadienyl rings of two crystallographically non-equivalent molecules in the same unit cell.

It is a common observation in x-ray diffraction studies of the structures of bis-cyclopentadienyl complexes that a shorter mean ring carbon-carbon bond length is associated with higher anisotropic thermal parameters for that ring. A particular example is bis-cyclopentadienyl titanium pentasulphide[9] where the two rings occupy axial and equatorial positions on a six-membered ring comprising the titanium and sulphur atoms. The mean carbon-carbon bond length is 1.381Å for the axial ring and 1.348Å for the equatorial ring. A rigid body analysis of the librations corresponded to angles of oscillation of ±5° and ±20° respectively.

---

†The experimental second moments are 1.2G^2 and 1.3G^2 at room temperature and 77K respectively. Thus no additional information could be obtained from line width or second moment studies except that the low value at 77K confirms the persistence of ring rotation (on the nmr time scale) at low temperature, and thus of the low barriers to rotation.

In the series of bis-cyclopentadienyl metal complexes studied by Prout and co-workers[7] the anisotropic thermal parameters were not analysable in terms of rigid body motions, which led these authors to suggest that static disorder, rather than thermal motion, was responsible for the spread in ring carbon-carbon bond lengths. For the molybdenum complex the mean bond lengths were 1.35Å and 1.38Å for the two rings on Mo(1) and 1.38Å and 1.39Å for those on Mo(2). While these results conveniently agree with the T_1 observations of one low barrier, two intermediate, and one high barrier these mean bond lengths are within 3σ of each other and the only meaningful conclusion perhaps is to assign the cyclopentadienyl ring with the shortest mean bond length [C(41) to C(45) in the notation of Ref. (7)] and largest thermal parameters as the ring with the lowest barrier. This ring is in the molecule with the staggered conformation but the description of the two crystallographically non-equivalent molecules as staggered and eclipsed is an oversimplification. If the angles of rotation of each cyclopentadienyl ring about the metal atom-ring centroid axis are considered then the mean difference in angle between the neighbouring carbon atoms of each ring is 13° for the "eclipsed" form at Mo(2) and 21° for the staggered molecule at Mo(1) (for the ideal conformations these angles would be 0° and 36°, respectively). In the triclinic phase of ferrocene the angle is about 9° which is largely dictated by intermolecular forces since the intramolecular potential barrier is very small. It does not seem possible to assign with certainty each of the barriers measured for bis-cyclopentadienyl molybdenum dichloride to individual rings or to draw definite conclusions as to the source of the barriers and their relationship to the conformation. The generally low values for these potential barriers to ring rotation indicate, however, that a dynamic process is occurring rather than static disorder.

The analogous complex bis-cyclopentadienyl titanium dichloride was studied by Holm and Ibers[10] using a progressive saturation method for obtaining T_1. A barrier of 2.1 ± 0.8 kJ mol^{-1} was reported. No T_1 minimum was observed but a change in line slope in a $\ln T_1$ vs $1/T$ plot occurred at about 320K and there was evidence for the existence of more than one correlation time. The crystal structure of this compound is triclinic with two molecules in the asymmetric unit, both with the staggered conformation.[11] The titanium compound should, therefore, exhibit the same behaviour as the molybdenum complex with four cyclopentadienyl rings occupying different sites and four (or three) different potential barriers to rotation.

Acknowledgments

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada. The sample of bis-cyclopentadienyl molybdenum dichloride was kindly supplied by Miss Gabriela Marmolejo. PGF acknowledges the award of a McGill University Graduate Research Fellowship.

References

1. P. Seiler and J. D. Dunitz, *Acta Cryst.*, **B35**, 1068 (1979).
2. F. Takusagawa and T. F. Koetzle, *Acta Cryst.*, **B35**, 1074 (1979).
3. P. Seiler and J. D. Dunitz, *Acta Cryst.*, **B35**, 2020 (1979).
4. A. Haaland and J. E. Nilsson, *Acta Chem. Scand.*, **22**, 2653 (1968).
5. A. J. Campbell, C. A. Fyfe, D. Harold-Smith and K. R. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **36**, 1 (1976).
6. J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956).
7. K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Cryst.*, **B20**, 2290 (1974).
8. R. L. Cooper and M. L. H. Green, *J. Chem. Soc.*, (A) 1155 (1967).
9. E. F. Epstein, I. Bernal and H. Köpf, J. Organomet. Chem., **26**, 229 (1971).
10. C. H. Holm and J. A. Ibers, *J. Chem. Phys.*, **30**, 885 (1959).
11. A. Clearfield, D. K. Warner, C. H. Saldamaga-Molina, R. Ropal and I. Bernal, *Can. J. Chem.*, **53**, 1622 (1975).