Tetrahedron Vol. 46, No. 6, pp. 1999-2008, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

Conformational Inversion in the Dodecahydrotriphenylene Radical Cation.

David V. Avila, Alwyn G. Davies*, and Maria L. Girbal.

Chemistry Department, University College London,
20 Gordon Street, London WC1H OAJ, U.K.

(*Received in UK* 29 *September* 1989)

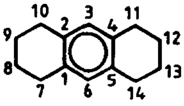
Abstract

The temperature dependence of the e.s.r. spectrum of the radical cation of dodecahydrotriphenylene (**2**$^{\cdot+}$) shows that the activation energy for inversion of the (benzo)cyclohexene ring is 4.8 kcal mol^{-1}, less than it is in the octahydroanthracene radical cation (**1**$^{\cdot+}$).

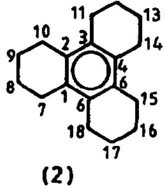
Introduction

Conformational inversion in the cyclohexene ring of a radical ion containing a benzocyclohexene moiety can in principle be studied by monitoring the temperature dependence of the hyperfine coupling of the exchanging axial and equatorial protons (equation 1), but as far as we can determine there is no report of this having been done for either a radical cation or radical anion. We describe here a variable temperature e.s.r. study of the radical cations of octahydroanthracene (**1**) and dodecahydrotriphenylene (**2**), which has provided the inversion barrier in (**2**$^{\cdot+}$).

(1)



(1)



(2)

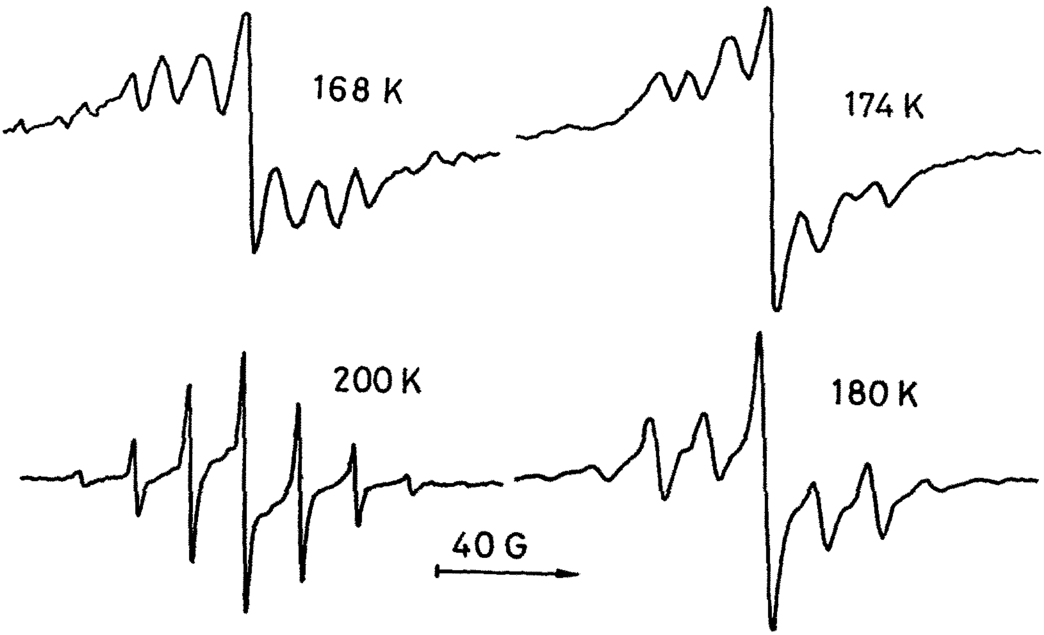


Figure 1. E.s.r. spectrum of (1$\dot{+}$) at various temperatures in CH_2Cl_2 (200 K) or CH_2Cl_2/ CF_2Cl_2 (other temperatures)

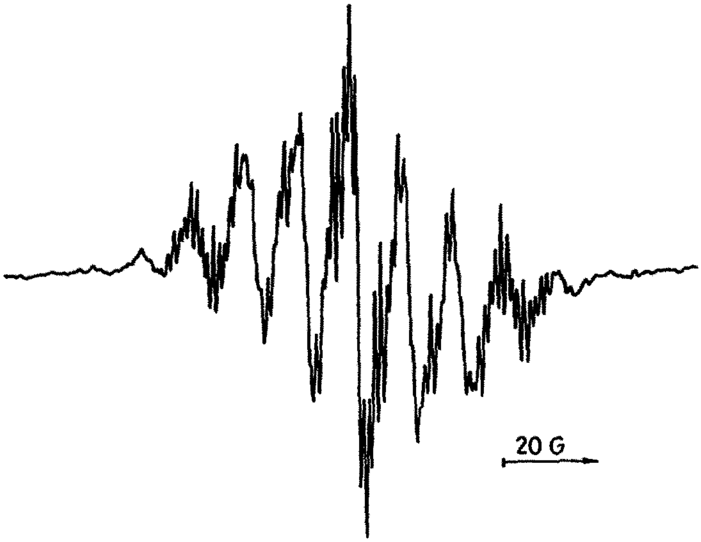


Figure 2. E.s.r. spectrum of (2$\dot{+}$) in CH_2Cl_2 at 200 K.

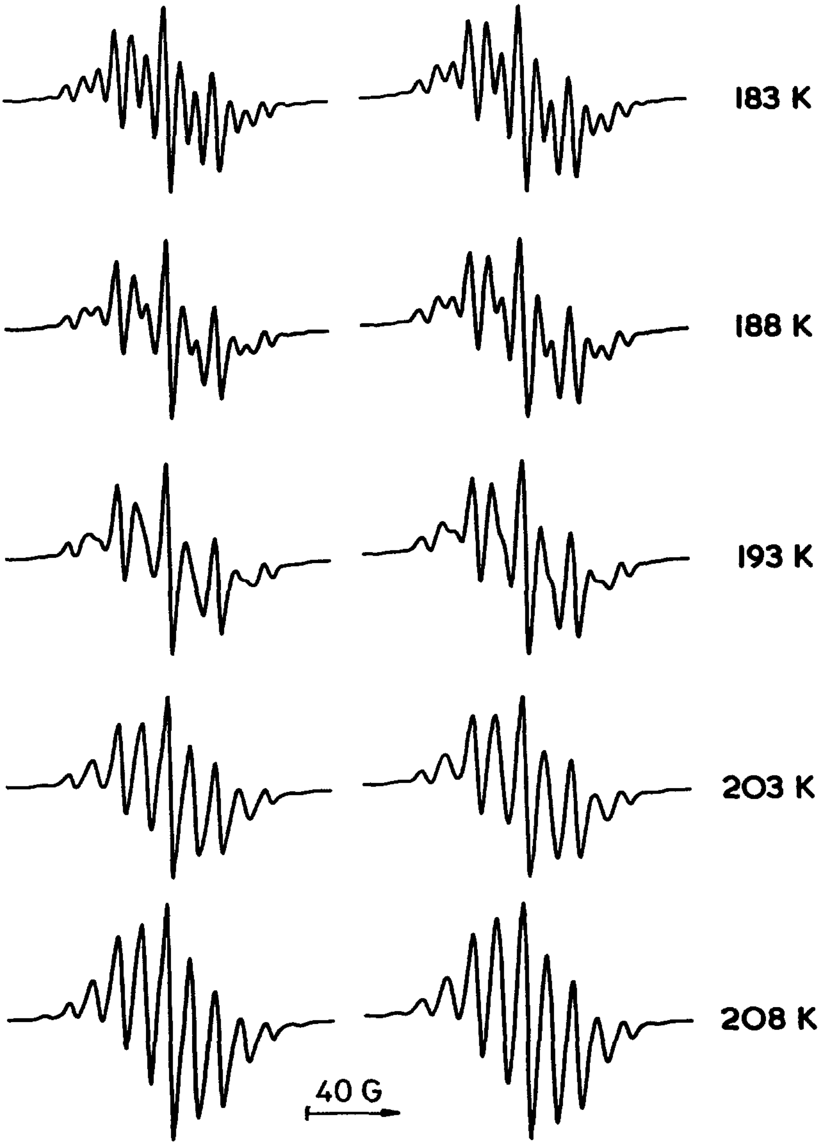


Figure 3. E.s.r. spectra (left) of (2$^{\cdot+}$) in CH_2Cl_2, and computer simulations (right).

Results

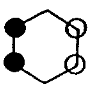
The e.s.r spectra of $(1\dot{+})$ [$\underline{a}(8H\beta)$ 15.5 G] and of $(2\dot{+})$ [$\underline{a}(12H\beta)$ 10.1 G] have been observed previously by Dessau and Shih[1] who oxidised (1) or (2) with cobaltic ion in trifluoroacetic acid in a rapid mixing flow system at room temperature, but this technique cannot readily be adapted for studies at low temperature. We have generated the radical cations by photolysis with Pyrex-filtered u.v. light of a static solution in the e.s.r. cavity of the appropriate hydrocarbon in dichloromethane containing aluminium chloride.

Octahydroanthracene (1) showed a spectrum of the radical cation $(1\dot{+})$ with $\underline{a}(8H\beta)$ 15.5 G, g 2.0029 (Figure 1). The spectrum of $(1\dot{+})$ showed no significant line-width effect down to the lowest temperature (190 K) which could be reached in this solvent, but with a mixture of dichloromethane and difluorodichloromethane, relatively poor spectra could be obtained down to 168 K. Alternate lines broadened at ca. 180 K and then split into separate signals (Figures 1) corresponding to $\underline{a}(4H\beta_{ax})$ 20.15 G and $\underline{a}(4H\beta_{eq})$ 10.85 G. Only the spectrum at 180 K was of sufficient quality to warrant simulation, and this gave a rate constant for axial-equatorial exchange of ca. 9.6×10^{7} s^{-1} at 180 K. If log A is taken to be 12.8 as it is for the dodecahydrotriphenylene radical cation (see below), this would correspond to an activation energy of ca. 4.0 kcal mol^{-1}.

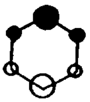
Dodecahydrotriphenylene (2) in dichloromethane at room temperature showed a spectrum of $(2\dot{+})$ with $\underline{a}(12H\beta)$ 10.24 G, $\underline{g}$ 2.0028, and at lower temperature a further splitting of ca. 1 G could be detected because of coupling to the γ-protons (Figure 2). Between ca. 213 K and 183 K alternate lines in the 13-line multiplet broadened and resolved into two signals so that at low temperature the spectra could be analysed in terms of $\underline{a}(6H\beta_{ax})$ 13.31 G and $\underline{a}(6H\beta_{eq})$ 7.17 G (Figure 3). Computer simulation of these spectra gave the rate constants for the ring inversion process which are shown in the Arrhenius plot in Figure 4, which is described by equation 2, where $R = 1.986 \times 10^{-3}$ kcal deg^{-1} mol^{-1}, and at 180 K, $k = 9.3 \times 10^{6}$ s^{-1}.

$$\log_{10}(k/s^{-1}) = (12.8 \pm 0.3)-(4.8 \pm 0.3)/2.303RT \qquad (2)$$

The 400 MHz ^{1}H n.m.r. spectrum of (2) in CHF_2Cl containing 20% CD_2Cl_2 was recorded down to 133 K. The methylene groups gave signals at δ 1.772 and 2.572, and these showed no sign of broadening and separating into separate signals for axial and equatorial protons even at the lowest temperature.[2]



(3)



(4)

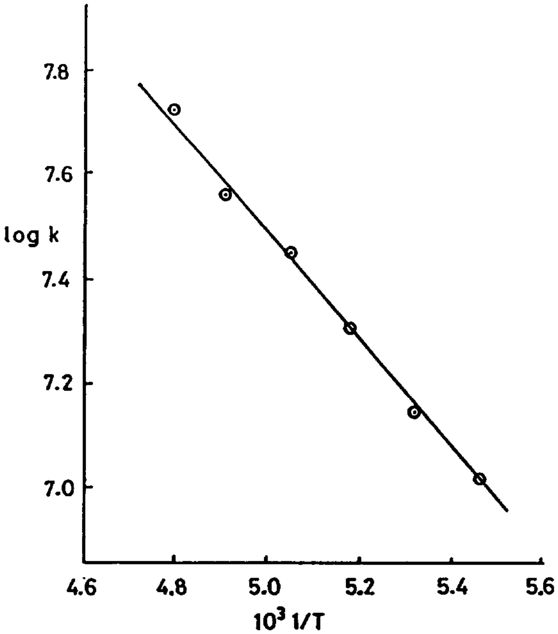


Figure 4. Arrhenius plot for the inversion of (**2**$\dot{+}$) (equation 2).

Discussion

The high value of $\underline{a}(H\beta)$ in (**1**$\dot{+}$) and the absence of any resolvable coupling to the protons in the aromatic ring shows that the 1,2,4,5-tetraalkylation has raised the energy of the ψ_A molecular orbital (3) above that of the ψ_S M.O. (4) so that the unpaired electron is located solely in ψ_A. For comparison the radical cation of durene shows $\underline{a}(12H\beta)$ 10.70 G, $\underline{a}$(2H-3,6) 0.8 G.[3] In (**2**$\dot{+}$), the ψ_A and ψ_S M.O.s should remain degenerate leaving equal electron distribution around the aromatic ring. For comparison, $Me_6C_6\dot{+}$ shows $\underline{a}$(18H) 6.45 G,[3] and $Et_6C_6\dot{+}$ shows $\underline{a}(12H\beta)$ 2.65, $\underline{a}(18H\gamma)$ 0.73 G at 253 K.[4]

The most interesting point to come out of these measurements however is that the barrier to ring inversion in the dodecahydrotriphenylene radical cation is apparently greater than that in the octahydroanthracene radical cation.

Dodecahydrotriphenylene (**2**) provides an interesting example of a family of compounds which has attracted much attention,[5] where steric interaction occurs between alkyl groups bonded to a planar framework. This might be expected to lead to correlated rotation between the alkyl groups in what has been termed a gear or cogwheel effect, but it appears that with simple alkyl groups, stepwise rather than correlated rotations usually occur.[6] We can find no record of (**2**) being discussed in this context.

We have investigated by molecular mechanics calculations (MM2) the potential energy profiles which are traced out when the cyclohexene moieties in (**1**) and in (**2**) undergo ring inversion.

We find in agreement with Koningsveld and Baas[7] that the two possible structures (*A*) and (*E*) of (**1**) with the cyclohexene rings in half-chair conformations have equal stability as shown in Figure 5. The two X-ray diffraction studies which have been carried out[7,8] have identified the centrosymmetric conformer (*A*) with a C_2 axis of symmetry.

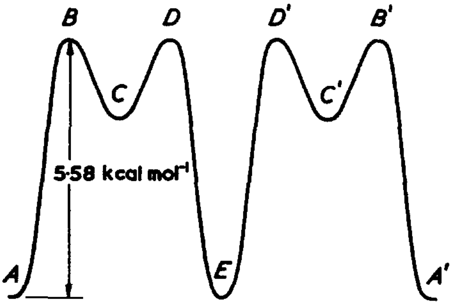
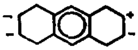


Figure 5. MM2-Derived energy profile for the inversion of a cyclohexene ring in octahydroanthracene (**1**).

Table 1. MM2 Steric energies and dihedral angles for the various conformations of (**1**) shown in Figure 5.

Conformation		**Steric energy**	**Dihedral angle/°** [a]		
		ΔE_s/kcal mol^{-1} [b]	3-2-10-9	6-1-7-8	7-8-9-10
A		0.00	+163.06	+164.41	-64.83
B		5.58	+178.48	-165.10	-31.57
C		3.84	+133.08	- 132.27	+1.92
D		5.57	-179.00	-164.49	+31.56
E		0.00	-163.91	-163.49	+64.82

[a] The positions are numbered as shown in (1). A positive angle indicates clockwise rotation. On the formulae, a positive sign indicates that the methylene group is above the plane of the benzene ring.

[b] Relative to the ground state structure *A* which was calculated to have a total strain energy E_s of 4.06 kcal mol^{-1}.

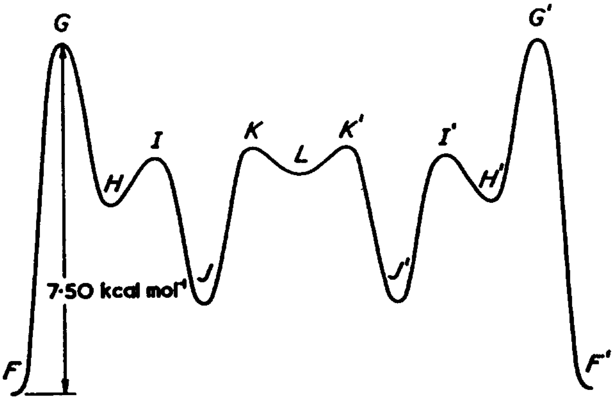
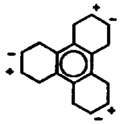
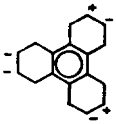
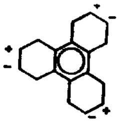
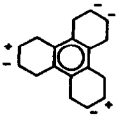


Figure 6. MM2-Derived energy profile for the inversion of a cyclohexene ring in dodecahydrotriphenylene (2).

Table 2. MM2 Steric energies and dihedral angles for the various conformations of (2) shown in Figure 6.

Conformation		**Steric energy**	**Dihedral angle/°**[a]		
		ΔE_s/kcal mol^{-1} [b]	3-2-10-9	6-1-7-8	7-8-9-10
F		0.00	+163.00	+164.06	-65.13
G		7.50	+163.44	-177.59	-26.60
H		4.15	+130.82	-129.43	-2.16
I		4.98	-137.43	+157.15	+38.15
J		1.62	-164.59	-163.39	+64.78
			2-3-11-12	5-4-14-13	11-12-13-14
K		5.24	-152.71	+136.57	-35.10
L		4.73	-130.75	+131.31	+1.61

[a] The positions are numbered as shown in (2). See also footnote [a] to Table 1.

[b] Relative to the ground state structure *F* which was calculated to have a total strain energy E_S of 11.83 kcal mol^{-1}.

Operation of the dihedral driver on one cyclohexene ring generated the potential energy profile shown in Figure 5, in which two semiplanar transition states (*B*) and (*D*) separate the half-chair reactants (*A*) and (*E*) from the boat intermediate (*C*) by an inversion barrier of 5.58 kcal mol^{-1}. Steric energies and some dihedral angles are given in Table 1. In cyclohexene itself (partially deuteriated) the activation enthalpy is found by n.m.r. to be about 5.3 kcal mol^{-1}, and the boat conformation is generally believed to be the transition state.[9,10]

A similar examination of (2) showed the most stable conformation (*F*) to be that with a C_3 axis of symmetry, minimising steric interactions between vicinal benzylic methylene groups. No complete X-ray diffraction study of (2) has yet been carried out[15], but the ligand (2) has this symmetry in the complex $[(\eta^6\text{-}2)Mn(CO)_3][BF_4]$.[16]

Inversion of one cyclohexene ring traces out the energy propile shown in *F* to *J* in Figure 6. The conformer (*J*) is now substantially less stable than (*F*) because of the destabilising interaction between two vicinal pairs of methylene groups. The boat conformer (*H*) again appears as an intermediate, and there is little change in the conformations of the other two rings, that is there is no cogwheel effect. The transition state (*G*) is semiplanar, but the second transition state (*I*) is not. Steric energies and some dihedral angles are given in Table 2.

Rotation of a second ring (*J* to *L*) then procedes over a second rather lower barrier. The complete lowest profile which could be located is shown in Figure 6 and detailed in Table 2. These calculations thus suggest a barrier of 7.50 kcal mol^{-1} for the exchange of axial and equatorial β-protons in 2, higher than that calculated for 1.

If (1) and (2) can be taken to be satisfactory models for ($1^{\cdot+}$) and ($2^{\cdot+}$) in the context of this ring inversion, this steric interaction between adjacent non-bonded methylene groups might provide the origin of the higher inversion barrier which we observe in ($2^{\cdot+}$). However there is a second, more subtle, factor that should be taken into account that would not be recognised by the molecular mechanics model.

The single crystal X-ray diffraction studies of octahydroanthracene (1)[7,8] show that the bonds from the central aromatic ring to adjacent methylene groups are not coplanar but subtend a dihedral angle of 3.8°.[17] If the structure of ($1^{\cdot+}$) is similar, and if this implies that the axes of the 2p orbitals on the adjacent aromatic ring atoms in the ψ_A M.O. (3) are not coparallel in the ground state, the activation energy for ring inversion might be reduced because during the inversion, the dihedral angle between these two A.O.s, which are in a locally bonding region of the M.O., becomes zero. A rather similar argument has been used to account for the deuterium isotope effect on the e.s.r. spectra of deuteriobenzene radical anions.[18] Even if the bonds to the central ring in ($2^{\cdot+}$) were not coplanar, the above effect would not be important because the ψ_S and ψ_A M.O.s. (3) and (4) are degenerate.

Experimental

Octahydroanthracene and dodecahydrotriphenylene were commercial products (Aldrich) and were purified by recrystallisation or chromatography before use.

^{1}H n.m.r. spectra at variable temperature were recorded on a Varian VXR 400 spectrometer, and e.s.r. spectra on a Varian E109 instrument with a 500 W high pressure mercury arc focussed on the cavity through a filter of Pyrex glass.

In order to obtain a set of spectra of ($2^{\cdot+}$) consistently without the small coupling illustrated in Figure 2, the spectra in Figure 3 were recorded with a modulation amplitude of ca. 2 G. The spectra were simulated using the ESRXN program (QCPE no. 209) using the parameters $\underline{a}(6H\beta_{ax})$ 13.31 and $\underline{a}(6H\beta_{eq})$ 7.17 G, and $\underline{a}$(12HY) 1.0 G, and a line width of 2.0 G.

Molecular mechanics calculation were carried out using the MM2 program (QCPE no. 423), taking for the C_{ar}-C_{ar} bonds, l_o 1.3937 Å and k_s 8.0667 mdyn Å^{-1}.[6]

Acknowledgements

We thank Dr. J.E. Anderson for carrying out the n.m.r. measurements, and Dr. C.H. Schiesser for assistance with the molecular mechanics calculations.

References

1. R.M. Dessau and S. Shih, *J. Chem. Phys.*, **1972**, *57*, 1200-1202.
2. If the separation between the signals for H_{ax} and H_{eq} were say 10 Hz, this would imply that the activation energy to ring inversion is less than 6.2 kcal mol^{-1}.
3. R.M. Dessau, S.Shih, and E.I. Heiba, *J. Am. Chem. Soc.*, **1970**, *92*, 412-413.
4. M.K. Carter and G. Vincow, *J. Chem. Phys.*, **1970**, *92*, 302-312.
5. U. Berg, T. Liljefors, C. Roussel, and J. Sandstrom, *Acc. Chem. Res.*, **1985**, *18*, 80-86.
6. J. Siegel, A. Gutierrez, W.B. Schweizer, O. Ermer, and K. Mislow, *J. Am. Chem. Soc.*, **1986**, *108*, 1569-1575.
7. H. van Koningsveld and J.M.A. Baas, *Acta Cryst.*, **1984**, *40C*, 311-313.
8. M.A. Wilson, A.M. Vassallo, M.I. Burgaer, P.J. Collin, B.W. Skelton,and A.H. White,. *Phys. Chem.*, **1986**, *90*, 3944-3948.
9. F.R. Jensen and C.H. Bushweller, *J. Am. Chem. Soc.*, **1969**, *91*, 5774-5782. F.A.L. Anet and M.Z. Haq, *J. Am. Chem. Soc.*, **1965**, *87*, 3147-3150.
10. As a check on the calculations, the energy profile for the inversion of cyclohexene itself was computed, and showed minimised strain energies for the chair, transition state, and boat structures of 4.19, 10.26, and 10.26 kcal mol^{-1} implying an inversion barrier of 6.07 kcal mol^{-1}. This is to be compared with the values in the literature of 5.97,[11] 6.1,[12] 6.39,[13] and 6.64[14] kcal mol^{-1}.

11. G. Favini, G. Buemi, and M. Raimondi, *J. Mol. Struct.*, **1968**, *2* 137-148.

12. R. Bucourt, *Topics in Stereochem.*, ed. E.L. Eliel and N.L. Allinger, **1974**, *8*, 159-244, esp. pp. 183-187.

13. N.L. Allinger and J.T. Sprague, *J. Am. Chem. Soc.*, **1972**, *94*, 5734-5747.

14. F.A.L. Anet and I. Yavari, *Tetrahedron*, **1978**, *34*, 2879-2886.

15. S.L. Chorghade, *Proc. Natl. acad. Sci. India.*, **1944**, *14A*, 30-36. F.Halla, H. H. Jagodzinski, and W.R. Ruston, *Acta Cryst.*, **1953**, *6*, 478-486.

16. L.H.P. Gommans, L. Main, and B.K. Nicholson, *J. Organomet. Chem.*, **1985**, *284*, 345-351.

17. Our MM2 calculation of the structure of (**1**) gave the dihedral angle 1-6-5-4 as 0.19°, but van Koningsveld and Baas' calculation[7] did reproduce this effect, giving the angle as 2.8°.

18. R.G. Lawler and G.K. Fraenkel, *J. Chem. Phys.*, **1968**, *49*, 1126-1139.