A Preference for the Boat Conformation in a *cis,cis*-Cyclodeca-1,6-diene Derivative

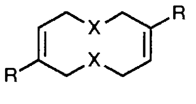
David P. G. Hamon* and Guy Y. Krippner

Organic Chemistry Department, The University of Adelaide, Adelaide SA 5000, Australia

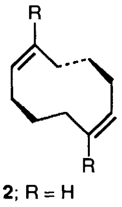
Ethyl *E,E*-6-(ethoxycarbonylmethyl)cyclodeca-1,6-dienylacetate is shown, by NMR spectroscopic evidence, to exist primarily in the boat conformation at room temperature.

Available experimental[1] and computational[2] evidence on the conformation of *Z,Z*-cyclodeca-1,6-diene **1** (X = CH_2) indicates a preference for a chair conformation **2** (C_{2h} symmetry) although a boat (or crown) conformation **3** (C_{2v} symmetry) is calculated to be not much higher in energy. Further studies on methylene substituted derivatives of **1** (X = substitued carbon) have led to the conclusion that a preference for the chair conformation is probably a general feature of this ring system.[3] Interesting observations on the NMR spectra of ethyl *E,E*-6-(ethoxycarbonylmethyl)cyclodeca-1,6-dienylacetate **4** provide evidence that this compound resides primarily in the boat (crown) conformation **5** (C_2 symmetry) and not the chair conformation **6** (C_i symmetry) at room temperature.

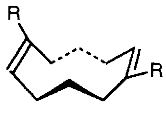
During a study of the synthesis of cyclodecyl compounds[4] we made the hydroxydiester **7** from the ketoester **8** by a crossed Claisen reaction utilising the anion[5] of ethyl acetate. Dehydration of this alcohol with thionyl chloride in pyridine and toluene below −7 °C gave a mixture of dienediesters from which one crystallised (m.p. 56–57 °C from light petroleum, 23% yield). Analytical and mass spectrometric data of this crystalline material were consistent with the isomeric diene structures. However, the proton-decoupled ^{13}C NMR spectrum (74.5 MHz) showed only nine carbon resonances and this is only consistent with the structures **4** (*E,E* or *Z,Z*. C_i or C_2 in each case) or **9** (*E,E*, or *Z,Z*. C_s or C_2 in each case). Both the ketoester **8** and the crystalline dienediester were subjected to NOE difference experiments. Irradiation of the resonances due to the methylene groups next to the ester moiety,† in each case, led to an enhancement of the resonance for the vinylic proton of 11–13%. These data show[6] that the vinylic protons are *cis* to the side-chain in both compounds. The structure **4** (*E,E*) was then assigned on the basis of a ^1H (300 MHz) COSY experiment, which showed that at least one of the ring allylic methylene protons (δ 2.03, m), which is coupled to the vinylic proton (δ 5.17, m) is also coupled to at least two other protons; its geminal neighbour (δ 1.78 m, also coupled to the vinylic proton, superimposed) and the higher field proton (δ 1.39, m). The protons of the other ring allylic methylene group [δ 2.37, dt, *J* 13.5 and 4.1 Hz, and δ 1.7(5), m, superimposed] are coupled to each other and to two higher field protons (δ 1.67, m, superimposed, and δ 1.39, m). Remaining in the spectrum are the absorptions for the ethyl group (δ 4.06, q, *J* 7.2 Hz, and δ 1.19, t, *J* 7.2 Hz) and the methylene group adjacent to the ester. It is this latter signal that is most intriguing. It is an AB quartet (δ 2.97 and 2.84, *J* 14.7 Hz). Clearly the protons of this methylene group appear to be diastereotopic.



1; R = H
4; R = CH_2CO_2Et, X = CH_2

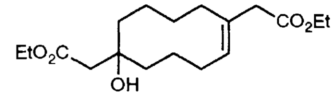


2; R = H
6; R = CH_2CO_2Et



3; R = H
5; R = CH_2CO_2Et

8



7

9

---

† *Spectroscopic data*: (*a*) ^1H 300 MHz NMR spectrum of compound **8**: δ 5.32 (t, *J* 8.5 Hz, 1H), 4.13 (q, *J* 7.2 Hz, 1H), 3.00 (s, 2H), 2.46 (br s, 2H), 2.34 (m, 2H), 2.14 (m, 4H), 1.6–1.9 (m, 6H), 1.26 (t, *J* 7.2 Hz, 3H). Irradiation of the singlet at δ 3.00. (*b*) Dienediester: irradiation of the AB quartet at δ 2.97 and 2.84.

The chair conformation **6** has a centre of symmetry and is, therefore, achiral. There is no reason to believe that, in this extended conformation, restricted rotation about the side chains could account for the non equivalence of the methylene protons adjacent to the ester groups. The boat conformation **5**, however, has planar chirality which might manifest itself if conformational inversion is slow on the NMR timescale. Interconversion of the conformers of *Z,Z*-cyclodeca-1,6-diene,[1] and some derivatives,[1,3] all of which prefer the chair conformation, is slow at room temperature and it is reasonable to assume that this applies to the dienediester **4** also. Variable-temperature NMR studies reveal that the diene-diester **4** is a dynamic system. At higher temperatures the AB quartet resonance and the multiplets for the ring protons collapse to broadened singlets. Coalescence of the signals occurs at about 325 K, which corresponds to a rate[7] k_c *ca.* 121 s^{-1} and to $\Delta G^{\ddagger}$[8] *ca.* 67 kJ mol^{-1}.

Molecular mechanics calculations support our proposal. The program[9] used calculates that the chair **2** and the boat **3** conformations of *Z,Z*-cyclodeca-1,6-diene **1** ($X = CH_2$) are about equal in energy. However, the program also calculates that for the dienediester **4**, the boat conformation **5** is some 8.7 kJ mol^{-1} more stable than the chair conformation **6**.

Clearly both the NMR data and the calculations are in agreement that this sytem prefers the boat conformation at room temperature. It is the unique combination of relatively restricted rotation in these systems and the chirality of the boat conformation of **4** that allows this to be observed using NMR spectroscopy.

D. P. G. H. wishes to thank Dr Manfred Christl, University of Würtzburg, for stimulating discussions.

Received, 29th June 1992; Com. 2/03443C

References

1 J. Dale, T. Ekeland and J. Schaug, *J. Chem. Soc., Chem. Commun.*, 1968, 1477; A. Almenningen, G. G. Jacobsen and H. M. Seip, *Acta Chem. Scand.*, 1969, **23**, 1495.

2 N. L. Allinger, M. T. Tribble and J. T. Sprague, *J. Org. Chem.*, 1972, **37**, 2423; O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, 1973, **95**, 4121.

3 B. W. Roberts, J. J. Vollmer and K. L. Servis, *J. Am. Chem. Soc.*, 1974, **96**, 4578.

4 D. P. G. Hamon and G. Y. Krippner, unpublished work.

5 M. W. Rathke, *J. Am. Chem. Soc.*, 1970, **92**, 3222.

6 V. Jacobsson, T. Norin, M. Weber and E. Tsankova, *Tetrahedron*, 1985, **41**, 2033 and references cited therein.

7 R. J. Kurland, M. B. Rubin and W. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

8 W. A. Thomas in *Annual Reports on NMR Spectroscopy*, ed. E. F. Mooney, 1968, vol. 1, p. 43.

9 PC-MODEL, Serena Software, Box 3076, Bloomington, IN, USA.