Tetrahedron Letters No. 36, pp. 3355 - 3356, 1971. Pergamon Press. Printed in Great Britain.

ON THE NON-EQUIVALENCE OF $-OCH_2-$ PROTONS IN SIMPLE CYCLOHEXANECARBOXYLIC ETHYL ESTERS

S. N. Balasubrahmanyam and M. Sivarajan
Department of Organic Chemistry
Indian Institute of Science, Bangalore, India

(Received in UK 22 June 1971; accepted for publication 4 August 1971)

Diethyl cis 1,3-dimethylcyclohexane-1,3-dicarboxylate (Ia) exhibits in its NMR spectrum[1] a symmetric thirteen line pattern (Figure 1) of four proton intensity in the $-OCH_2-$ region which appeared to result from the overlap of some of the lines of a sixteen line pattern to be expected of the AB part of an ABX_3 system[2]. The corresponding trans diester (Ib) exhibits a normal quartet of four proton intensity. The equivalence in the trans case requires that the rate of sweep of the environment of the $-OCH_2-$ protons must be faster than the rate of ring inversion at the temperature of measurement. The non-equivalence in the cis case may have either of two possible origins: i) Restricted rotation about the $O-CH_2$ bond [this requires the cis ester to have the conformation (Ia) and implies that the non-equivalence would be destroyed on removing the restriction to free rotation[3]. ii) Intrinsic asymmetry of the type

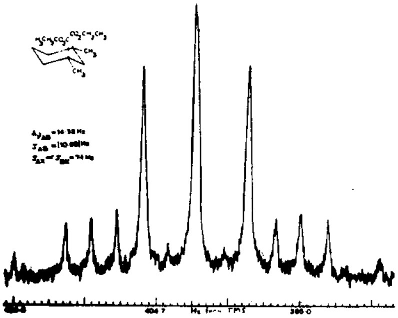
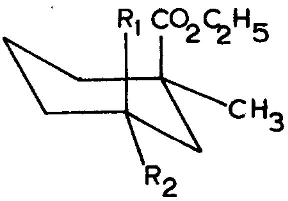


Figure 1



I a : $R_1 = CO_2C_2H_5$; $R_2 = CH_3$
b : $R_1 = CH_3$; $R_2 = CO_2C_2H_5$
c : $R_1 = CO_2CH_3$; $R_2 = CH_3$

exemplified by 3,3-dibenzylphthalide[4] [this assumes that the asymmetry is transmitted across the carboxyl group].

We hoped to resolve the question by a study of the NMR spectrum of diethyl *cis* 1-methylcyclohexane-1,3-dicarboxylate and diethyl *cis* cyclohexane-1,3-dicarboxylate in both of which the ethoxycarbonyl groups may be expected to be predominantly equatorial with no restriction of rotation. These diesters did not exhibit AB non-equivalence of the $-OCH_2-$ protons confirming that the non-equivalence in the case of the diester (Ia) was due to restriction of rotation. As expected, non-equivalence was found for the single $-OCH_2-$ pair in ethyl *cis* 1-methoxycarbonyl-1,3-dimethylcyclohexane-3-carboxylate (Ic) (Figure 2)[1].

That this type of non-equivalence in ethyl diesters can be diagnostic of *syn* axial relationship [with the approximate distance prevailing in conformation (Ia)] is exemplified by the case of diethyl 4,5-benzo-2,3:6,7-bishomotropane-2,7-dicarboxylate recently discussed by Sugimura *et al.*[5]

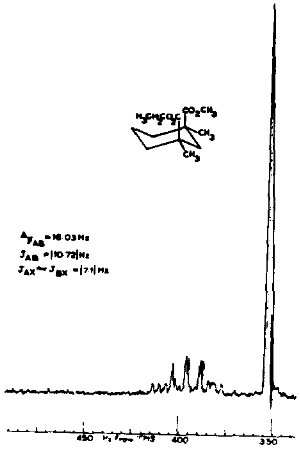


Figure 2

We are grateful to Professor D.K.Banerjee for his kind interest and encouragement and to Drs.A.J.Boulton, G. Nadamuni, G. Subrahmanyam and C.L. Khetrapal for discussions.

References and Footnotes

1. Spectra were recorded at 100 MHz for carbon tetrachloride solutions.
2. L.M.Jackman and S.Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, Second Edition, 1969, p.114.
3. *E.g.* the decalin-10-carboxylic ethyl ester systems studied by W.L.Meyer, D.L.Davis, L.Forter, A.S.Levinson, V.L.Sawin, D.C.Shew and R.F.Weddleton, *J.Amer.Chem.Soc.*, **87**, 1573 (1965).
4. F.A.Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York and London, 1969, p.163 *et seq.*; T.D.Coyle and F.G.A.Stone, *J.Amer.Chem.Soc.*, **83**, 4138 (1961).
5. Y.Sugimura, N.Soma and Y.Kishida, *Tetrahedron Letters*, 91 (1971).