Tetrahedron Letters No. 4, pp 277 - 280, 1972. Pergamon Press. Printed in Great Britain.

# EXPERIMENTAL PROOF OF DIAXIAL $^4J$ LONG RANGE COUPLING CONSTANTS IN NMR SPECTRA OF HALOGENOCYCLOHEXANONES AND HALOGENODECALONES.

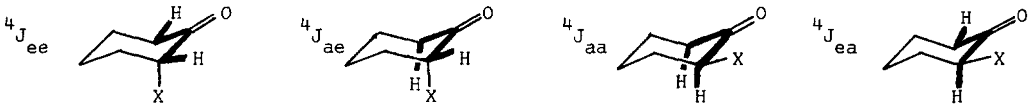
C. Cuvelier, R. Ottinger and J. Reisse[x]

*Université Libre de Bruxelles, 50, av. F.-D. Roosevelt, 1050 Bruxelles, Belgique*

(Received in UK 6 December 1971; accepted for publication 23 December 1971)

Four kinds of $^4J$ coupling constants between α and α' protons may exist in an α-monosubstituted cyclohexanone (fig. 1).

FIG. 1.



Many examples of $^4J_{ee}$ are known (1-7), the absolute value of this coupling constant being of the order of 1-2 Hz.

The importance of such a long range coupling constant may be correlated with particular W or M path of Meinwald and Lewis (8) even if it is not sure that the mechanism of this coupling implies the antilobes of the C-H bonds (9).

The literature gives some examples of $^4J_{aa}$ coupling constants (10,11,12) but Jefford and Waegell (14) claim that in each case a slight ambiguity remains concerning 1°) the exact geometry of the molecule or 2°) the attributions of the NMR signals.

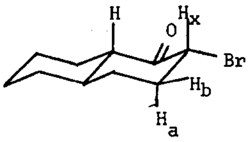
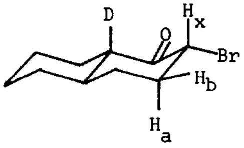
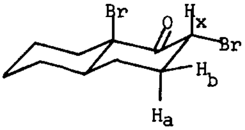
Recently, Richer and all. (13) give evidence of a $^4J_{aa}$ coupling in a polyalkylated bromocyclohexanone. It may be observed that in this molecule also, the interaction between the t-butyl group and the vicinal two methyl groups may introduce some deformations in the molecule.

The bromo-1-decalones are good systems to study the $^4J$ problem essentially because the double chair structure may be considered as sure and also because the trans fused molecules are rigid.

The table I gives results concerning three bromo-trans-1-decalones.

First of all, it is important to note that the "extra" splitting of each component of the X part of the ABX[*] systems studied in this paper is generally easy to observe in $C_6H_6$ as solvent but not in $CCl_4$. In this last solvent, the X signal is frequently not resolved. This broadening may be due to a virtual coupling between $H_X$ and $H_4$ protons (15,16,17). Such a virtual coupling may be present in $CCl_4$ but not in $C_6H_6$. It is well known that the solvent effect on chemical shifts is very important for ketones and halogenoketones when such compounds are used as a solute in $CCl_4$ and $C_6H_6$ (18).

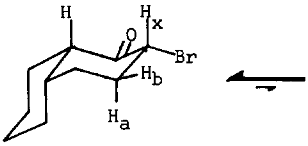
TABLE I (solvent $C_6H_6$)

| | | $J_{AX} + J_{BX}$ Hz | $^4J$ Hz |
|---|---|---|---|
| I |  | 18,8 | $\|0,9\|$ |
| II |  | 18,9 | 0 |
| III |  | 19,7 | 0 |

The spectrum of I and comparison between spectra of I on the one hand and II and III on the other hand are evident proofs of $^4J_{aa}$ in a non distorted chair cyclohexanic structure.

The values of $|J_{AX} + J_{BX}|$ directly observed on the X part of the ABX system (ignoring the long range coupling ) give a very good indication of axial or equatorial orientation of the bromine atom. Using this probe (and also IR and UV spectroscopy) we consider the fused cis system of table II as an equilibrium displaced toward the only indicated conformation.

TABLE II (solvent $C_6H_6$)

| | | $J_{AX} + J_{BX}$ Hz | $^4J$ Hz |
|---|---|---|---|
| IV |  | 18,4 | $\|0,9\|$ |

---

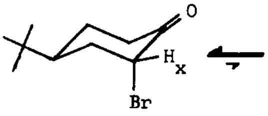
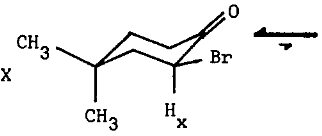
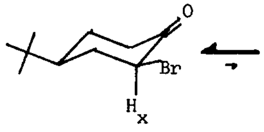
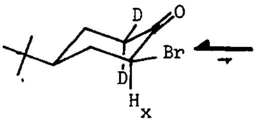
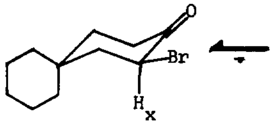
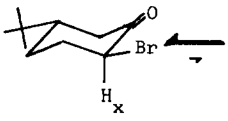
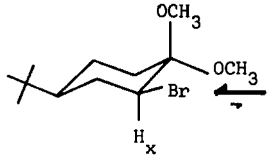
[*] It is impossible to observe the AB part of ABX system which is superimposed on the other absorptions. It is thus very difficult to make a complete analysis of the spin system but the first order analysis may be safely used to determine long range coupling constants in the systems studied here because of the very small value of $^4J$.

IV must thus be considered as further evidence of $^4J_{aa}$ coupling. In this case, experimental difficulties precluded the preparation of the 10-deuterated molecule.

The results obtained in 1-decalone series are extended to cyclohexanone series (tableIII). All systems listed in table III exist as equilibria between two chair conformations but it is easy to see, using the $J_{AX} + J_{BX}$ probe, that for each system the equilibrium is greatly displaced toward the only indicated conformation.

V is illustrative of $^4J_{ee}$ and VI - X give positive and negative proofs clearly indicating $^4J_{aa}$ coupling. The occurence of $^4J$ coupling in compounds IX and X and the absence of long range coupling in VII prove that the observed coupling is not of the $H_2 \ldots H_4$ type.
From these results we infer that in all the systems studied here the long range coupling perturbing the $H_x$ signal is only of the αα' type (9).

TABLE III (solvent $C_6H_6$)

| | | $J_{AX} + J_{BX}$ Hz | $^4J$ Hz | | | $J_{AX} + J_{BX}$ Hz | $^4J$ Hz |
|---|---|---|---|---|---|---|---|
| V |  | 5,9 | $\lvert 1,8 \rvert$ | IX |  | 18,8 | $\lvert 0,6 \rvert$ |
| VI |  | 18,8 | $\lvert 0,9 \rvert$ | | | | |
| VII |  | 18,7 | 0 | X |  | 18,7 | $\lvert 0,8 \rvert$ |
| VIII |  | 18,7 | $\lvert 1,0 \rvert$ | XI |  | 17,1 | 0 |

In all our compounds we have never observed $^4J$ coupling such as $^4J_{ea}$ or $^4J_{ae}$ between α and α' protons. If we use the classical separation of $^4J$ in σ and π contributions (9), the value of $^4J_{aa}$ is probably due to a contribution of $^4J_{\pi}$.
We support this interpretation by the study of the NMR spectra of compound XI. In this case, $^4J_{aa}$ is zero, probably because of the absence of $p_z$ orbital on $C_1$.

The absolute value of the $^4J_{aa}$ coupling constant is remarkably constant in all the derivatives if we except IX. We have no explanation for the smaller value of $^4J$ observed in this case. The many examples cited in this paper clearly confirm the importance of the $^4J_{aa}$ coupling constant in derivatives of cyclohexanone. **Finally** , we have studied 2-bromocyclohexanone itself. An extra splitting of the $H_X$ signal (J = 1,4 Hz) is clearly observed. We have not the definitive proof that this extra splitting is due to $H_2$-$H_6$ coupling only (a $^4J_{2e-4e}$ remains possible). If the observed J is effectively an average value between $^4J_{ee}$ and $^4J_{aa}$, it is easy to see that the relative signs of $^4J_{aa}$ and $^4J_{ee}$ must be the same (in $C_6H_6$ as solvent, it is well known that the mole fractionsof each conformation are practically equal).

ACKNOWLEDGMENTS. The authors are indebted to F.R.F.C. for its financial support, to I.R.S.I.A. for a grant (C.C.), and to Professor G. Chiurdoglu for his interest.

BIBLIOGRAPHY.

1) A. Rassat, C.W. Jefford, J.M. Lehn and B. Waegell, *Tet. Letters* **5**, 233 (1964).
2) B. Waegell, *Bull. Soc. Chim. Fr.*, 855 (1964).
3) H. Durr, G. Ourisson and B. Waegell, *Ber.* **98**, 1858 (1965).
4) H. Piotrowska, W. Wojnarowski, B. Waegell and G. Ourisson, *Bull. Soc. Chim. Fr.*, 3573 (1965).
5) J.P. Zahra, C.W. Jefford and B. Waegell, *Tetrahedron* **25**, 5087 (1969).
6) B. Waegell, *Bull. Soc. Chim. Fr.*, 844 (1964).
7) W. Wojnarowski and G. Ourisson, *Bull. Soc. Chim. Fr.*, 219 (1967).
8) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.* **83**, 2769 (1961).
9) M. Barfiel and B. Chakrabarti, *Chem. Rev.* **69**, 757 (1969).
10) P. Laszlo and J.I. Musher, *Bull. Soc. Chim. Fr.*, 2558 (1964).
11) B. Lacoume, *Bull. Soc. Chim. Fr.*, 3496 (1967).
12) M. Anteunis, N. Schamp and H. De Poorter, *Bull. Soc. Chim. Belges* **76**, 541 (1967).
13) J.C. Richer et N. Baskevitch, *Bull. Soc. Chim. Belges* **80**, 459 (1971).
14) C.W. Jefford and B. Waegell, *Bull. Soc. Chim. Belges* **79**, 427 (1970).
15) E.W. Garbisch, *J. Am. Chem. Soc.* **86**, 1780 (1964).
16) E.W. Garbisch, *J. Org. Chem.* **30**, 2109 (1965).
17) J.I. Musher and E.J. Corey, *Tetrahedron* **18**, 791 (1962).
18) J.D. Connolly and R. McCrindle, *Chem. Ind.*, 379 (1965).