ON THE MAGNITUDE AND SIGN OF THE $^5$J METHOXY-PROTON COUPLING IN 2,4-DIBROMO-ANISOL

H. Angad Gaur and J. Vriend

Department of Technical Physics, Technische Hogeschool, Delft (The Netherlands)

and

W. G. B. Huysmans

Central Research Institute of AKU (Algemene Kunstzijde Unie N.V.) and Affiliated Companies, Arnhem (The Netherlands)

Current literature (1-11) devotes much attention to long range coupling constants. Generally, the magnitude of the long range coupling can be easily determined by assuming first order splitting. However, access to the relative sign is more difficult and possible only in some cases (1,3, 10). In connection with the above we would like to report our results of spin-spin interactions via five and six bonds in 2,4-dibromo-anisol (DBA).

The chemical shift values and the coupling constants of DBA are given in TABLE I. FIG. 1a and 1b show the 60 MHz spectrum of the sample. By comparing the absolute values of the coupling constants between the ring protons, determined from FIG. 1a, with values reported for this in literature (12,13), the various groups of resonances were assigned to the corresponding protons in the molecule.

The doublet signal of the $OCH_3$ protons (FIG. 1b) is due to coupling with the ortho ring proton $H_A$. The quintet structure of the resonances of proton $H_A$ (FIG. 1d) is caused by coupling with proton $H_C$ (FIG. 1c) and with the methoxy protons. This is proved by decoupling the ring proton spectrum from the methoxy protons (FIG. 1e and 1f). The $H_A$ quintets become doublets (FIG. 1f), thus showing the coupling between the protons $H_A$ and $H_C$. At the same time the resonances of proton $H_B$ "wiggle" better. This is an indication for a weak coupling with the methoxy protons. In TABLE I an estimate of the magnitude of this coupling is given. The resonances of proton $H_C$ remain unchanged.

The relative signs of the coupling constants between the ring protons were determined by means of Triple Resonance. For that purpose the resonances of the ring protons were decoupled from
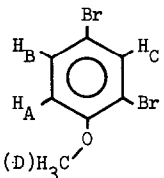
the OCH$_3$ group. Simultaneously the following peaks were irradiated successively:

1. The high-field doublet of H$_A$ (peaks 11 and 12, FIG. 1e). Then the high-field doublet of proton
   H$_C$ was decoupled. Therefore J$_{AB}$ and J$_{BC}$ have the same sign.

2. The high-field peak of proton H$_B$ (peak 8). The high-field resonance of each of the H$_C$ doublets
   (peaks 2 and 4) is split. So **J$_{AB}$ and J$_{AC}$ have the same sign.**

From the above it follows that the coupling constants between the ring protons all have the same
sign.

<div align="center">

TABLE I

Chemical shift values and coupling constants of DBA

</div>

| Compound (DBA) | Protons | Chemical shift [a] ($\delta$ in ppm) | Coupling constants [a] (in Hz) |
|---|---|---|---|
| | A | 6.65 | J$_{AB}$ = ± 8.77 |
| | B | 7.27 | J$_{AC}$ = ± 0.23 |
| | C | 7.59 | J$_{BC}$ = ± 2.38 |
| | D | 3.80 | J$_{AD}$ = ∓ 0.33 |
| | | | $\|J_{BD}\| \lesssim 0.1$ |

Structure diagram: benzene ring with Br (top), H$_B$ and H$_C$ (upper positions), H$_A$ and Br (lower positions), and (D)H$_3$C-O (bottom).

a) The spectra were recorded at room temperature from 9 (w/w) % deoxygenated solutions in CCl$_4$.
   The spectrometer was a Varian DA 60-IL. The chemical shift values (from TMS, $\delta$ = 0 ppm) are
   accurate to within ± 0.01 ppm and the coupling constants to within ± 0.02 Hz.

The relative sign of the OCH$_3$-H$_A$ coupling was determined by means of Double Resonance (DR).
FIG. 2a shows the H$_B$ resonances before DR. Upon irradiation of the high-field resp. the low-field
peak of the OCH$_3$ doublet, the low-field (FIG. 2b) resp. the high-field doublet (FIG. 2c) of the
H$_B$ resonances sharpens and forms "wiggles": in other words, they are decoupled. Therefore J$_{AD}$ and
J$_{AB}$ have different sign.

In various aromatic molecules it appears that all H-H coupling constants between the ring
protons have the same sign (12-14). Furthermore Buckingham and McLauchlan (15) have shown that
the J$_{HH}$ (ortho) value in p-nitrotoluene is positive. It seems likely that this also applies in
our case. Therefore all ring proton coupling constants are positive in DBA. Consequently the
methoxy-proton coupling with the ortho ring proton is negative.

In DBA we expect the rotation of the OCH$_3$ group around the oxygen-aromatic carbon axis to be
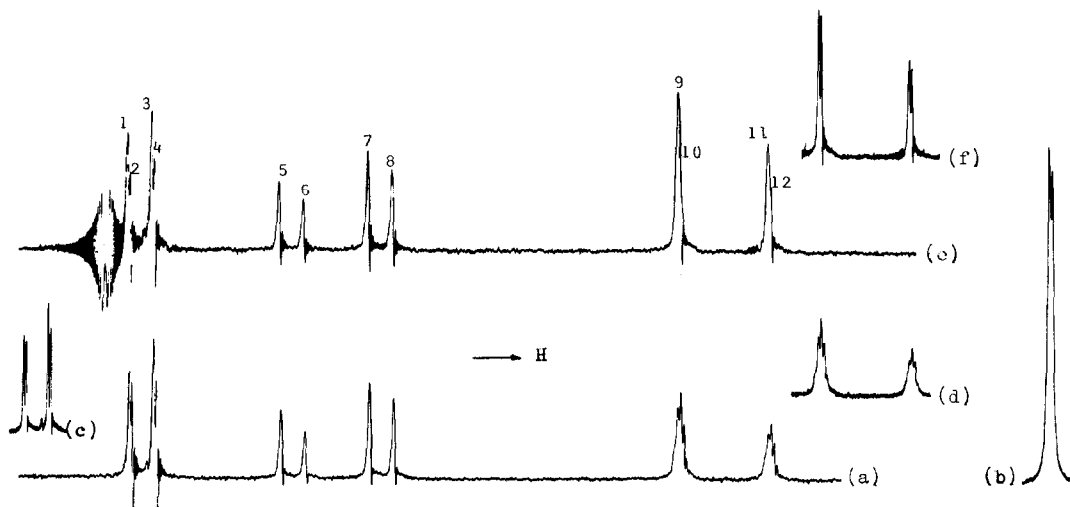
FIG. 1

The 60 MHz spectrum of the ring protons (a) and the methoxy protons (b) of DBA at room tem-
perature. The spectrum of proton $H_C$ (c) and of proton $H_A$ (d) at slow sweep rate ($\sim$ 1 Hz/mi-
nute). (e) and (f). The ring proton spectrum decoupled from the methoxy group. In (f) the
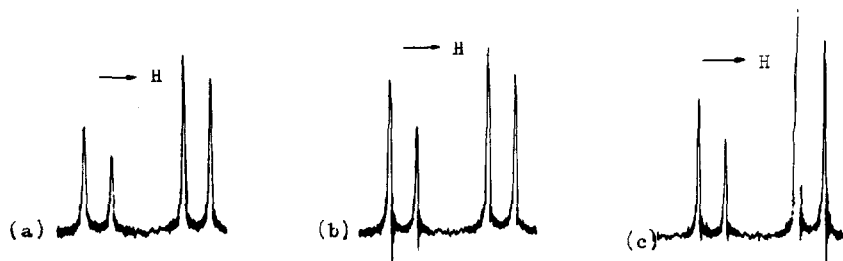$H_A$ resonances are recorded at a very slow sweep rate ($\sim$ 1 Hz/minute).



FIG. 2

The spectrum of proton $H_B$. (a) Unperturbed. (b) The low-field $H_B$-doublet is decoupled upon
irradiation of the high-field peak of the $OCH_3$ resonances. (c) The high-field $H_B$-doublet
is decoupled upon irradiation of the low-field peak of the $OCH_3$ resonances.

somewhat restricted due to interaction with the neighbouring ring bromide-substituent. Then on an

average the $O-CH_3$ axis should be mainly in the plane of the aromatic ring with the methyl group

pointing towards the ortho ring proton. Obviously this situation is favourable for the coupling

between the $OCH_3$ protons and the H (ortho) proton (here $|J_{AD}| = 0.33$ Hz), because in cases where

the $OCH_3$ group rotates freely around the oxygen-aromatic carbon axis, the coupling is hardly ob-

servable or not all (5,6,11). This we see clearly in 4-bromo-anisol and 1,4-dimethoxy-2,6-dimethyl-

phenol, where the magnitude of this coupling is 0.18 (± 0.03) Hz – obtained from decoupling experi-

ments – and respectively 0.15 (± 0.03) Hz – obtained from a poorly resolved $OCH_3$ triplet – (16).

The coupling of the $OCH_3$ protons with the meta ring proton is estimated at 0.1 Hz.

REFERENCES

1. S. Sternhell, Rev. Pure Appl. Chem. 14, 15 (1964) and references cited herein.

2. D. T. Witiak, P. B. Patel and Y. Lin, J. Am. Chem. Soc. 89, 1908 (1967).

3. G. Kotowycz and T. Shaefer, Canad. J. Chem. 44, 2743 (1966).

4. G. P. Newsoroff and S. Sternhell, Aust. J. Chem. 21, 747 (1968).

5. S. Forsén, J. Phys. Chem. 67, 1740 (1963).

6. S. Forsén, B. Åkermark and T. Alm, Acta Chem. Scand. 18, 2313 (1964).

7. V. F. Bystrov and A. U. Stepanyants, J. Mol. Spectroscopy 21, 241 (1966).

8. M. Barfield and D. M. Grant, Advances in Magnetic Resonance Vol. I, p. 149, edited by
   J. S. Waugh, Academic Press, London (1965).

9. W. H. de Jeu, Ph. D. Thesis, (1969), Delft, University of Technology.

10. W. G. B. Huysmans, J. G. Westra, W. J. Mijs, H. Angad Gaur, J. Vriend and J. Smidt,
    Tetrahedron Letters 4345 (1968).

11. R. W. Crecely, K. W. McCracken and J. H. Goldstein, Tetrahedron 25, 877 (1969).

12. H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, J. Am. Chem. Soc. 79, 4596 (1957).

13. D. M. Grant, R. C. Horst and H. S. Gutowsky, J. Chem. Phys. 38, 470 (1963).

14. J. Martin and B. P. Daily, J. Chem. Phys. 37, 2594 (1962).

15. A. D. Buckingham and K. A. McLauchlan, Proc. Chem. Soc. 144 (1963).

16. Unpublished results, obtained by the authors.