BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1439 (1971)

Conformational Factors Affecting the NMR Chemical Shifts of Nuclear Protons in Some Diarylmethanes

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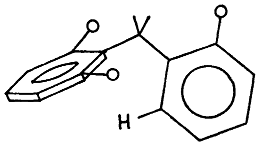
(Received October 12, 1970)

We have been interested in the study of conformational properties of diphenylmethanes (DPM) and have proposed[1] that a number of tri-*ortho*-substituted DPM exist predominantly in a conformation (I) where the *ortho* aromatic hydrogen lies below the adjacent ring.

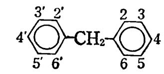


(I)

NMR data provide useful information on the conformation. In fact the shielding on the *ortho* positions, due to the ring current[2] of the adjacent nucleus, is a function of molecular conformation.[1] Some NMR data on variously substituted DPM, which appeared recently in this Journal,[3] can be interpreted as a further support of our previous results.

In Table 1 are collected the NMR chemical shifts of *ortho* aromatic protons for a number of tri-*ortho*-substituted DPM derivatives taken from Suzuki's work[3] together with our data. In tri-*ortho*-substituted DPM the *ortho* nuclear proton appears sensibly shielded with respect to the mono-substituted derivatives (Table 1, compounds 1 and 2). This can be accounted for by assuming that the tri-*ortho*-substituted compounds exist predominantly in form I where the *ortho* aromatic hydrogen lies below the adjacent ring. Other conformations become disfavored in this case because of the repulsive interaction between the *ortho* substituents and the π-electron cloud of phenyl ring.

Table 1. Chemical shifts of *ortho* and *para* nuclear protons in DPM derivatives

		Chem. shift (δ,CCl_4) H_{ortho}	H_{para}	Δ[a] (ppm)	Ref.
1	2-Me	7.12	7.12		b
2	2-Cl	7.15	7.15		b
3	2,3,5,6-Me	7.08	7.08		b
4	2,6-C1,2′-Me	6.20	6.92	0.63	b
5	2,3,5,6,2′-Me	6.42	7.00	0.41	1
6	2,4,6,2′,5′-Me	6.28	6.97	0.55	1
7	2,3,5,6,2′5′-Me	6.22	6.92	0.61	1
8	2,4,6,2′,3′,4′,5′-Me	6.00		0.83	3
9	2,3,4,6,2′3′,4′,5′-Me	6.01		0.82	3
10	2,3,5,6,2′,3′,4′,5′-Me	5.99	6.80	0.84	3
11	2,3,4,5,2′,3′,4′,5′,6′-Me	6.06		0.77	3
12	2,3,4,6,2′,3′,4′,5′-Me,5-Cl	6.04		0.79	3
13	2,3,5,6,2′,3′,4′,5′-Me,4-Cl	6.00		0.83	3
14	2,3,5,6,2′,4′,5′-Me,4-Cl	6.15		0.67	3
15	2,4,5,2′,3′,4′,6′-Me,3,5′-Cl	6.23		0.60	3
16	3,4,5,2′,3′,5′,6′-Me,2,4′-Cl	6.14		0.69	3

a) calculated as the difference between H_{ortho} value and the chemical shift of pentamethylbenzene nuclear proton (6.83 δ).

b) this work.

The magnitude of the shielding effect observed for tri-*ortho*-substituted compounds (0.5—0.8 ppm) compares fairly well with the theoretical shielding value calculated for conformer I through the Johnson and Bovey tables.[2] Considerably lower shielding values are calculated for other (skew) conformations. The shielding effect could be calculated as the difference between the chemical shift values of *ortho* and *para* nuclear protons since the latter are unperturbed from the adjacent ring diamagnetic current. However, this is not always possible for the compounds in Table 1 and the shielding has been computed taking the pentamethylbenzene nuclear proton as reference. The new data[3] seem to be in substantial agreement with ours and appear to support our interpretation.

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1) G. Montaudo, S. Caccamese, P. Finocchiaro, and F. Bottino, *Tetrahedron Lett.*, **1970**, 877.

2) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

3) H. Suzuki, This Bulletin, **42**, 2618 (1969).