

**^1H AND ^{13}C NMR SPECTRA AND INDO CALCULATIONS
OF 2,2'-DIFURYLMETHANE, 2-BENZYL-FURAN,
AND DIPHENYLMETHANE**

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Calculated INDO charges for 2,2'-difurylmethane, 2-benzylfuran, and diphenylmethane correlate well with NMR shifts of ^1H hydrogen atoms and ^{13}C carbon atoms of the furan ring. A good qualitative agreement was also found between the theoretically expected and experimentally obtained data on electrochemical attack of diphenylmethane.

At present we are concerned with electrochemical oxidation of 2,2'-difurylmethane (*I*) and 2-benzylfuran (*II*); since a paper has been published¹ dealing with electrochemical acetoxylation of a series of aromatic compounds including diphenylmethane (*III*), the opportunity arose to compare the electrochemical and NMR behaviour of the structural analogues *I-III*. During our work we found electrochemical oxidation of *I* and *II* to proceed in a quite different and very complicated manner. Although all the isolated products have not been so far identified, it can be stated with certainty that the principal reaction is not an anodic substitution as described¹⁻³ for *III*. For this reason the results so obtained could not be incorporated in the work present.

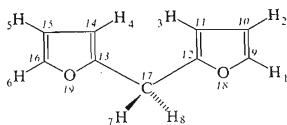
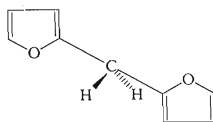
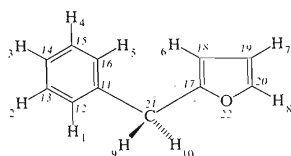
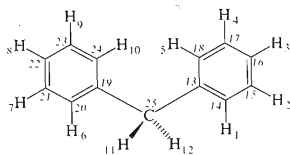
EXPERIMENTAL

2,2'-Difurylmethane⁴, 2-benzylfuran⁵⁻⁷, and diphenylmethane⁸ were prepared according to the procedures described. Calculations were performed using the standard program⁹, the bond lengths and bond and dihedral angles were taken from⁹⁻¹¹. The ^1H and ^{13}C NMR spectra were measured on an instrument Varian XL-100 CW employing the technique with CAT. 40% solutions in perdeuterioacetone were measured at 37°C with TMS as the standard. For the ^{13}C -NMR measurements the frequency of 25.2 MHz was applied.

RESULTS AND DISCUSSION

In order to facilitate the calculations, we assumed the carbon system to be planar for all the substances studied. For *I*, two conformations, as shown below (along

with the numbering of the atoms), were taken into account. The results were found to be virtually equal for the two cases.

*Ia**Ib**II**III*

The values of the INDO charges at the atoms are summarized in Table I for both conformations of *I* treated. Analogous results for the compounds *II* and *III* are

TABLE I

INDO Charges for the *a* and *b* Conformations of 2,2'-Difurylmethane and the Corresponding ^{13}C or ^1H -NMR Shifts (ppm)

Atom	INDO charge		NMR shift	Atom	INDO charge		NMR shift
	<i>a</i>	<i>b</i>			<i>a</i>	<i>b</i>	
1	-0.008	-0.019	7.324	10	-0.022	-0.032	106.67
2	-0.017	-0.005	6.292	11	-0.069	-0.059	110.60
3	0.015	0.005	6.047	12	0.168	0.159	151.79
4	0.015	0.019	6.047	13	0.168	0.169	151.79
5	-0.017	-0.018	6.292	14	-0.069	-0.062	110.60
6	-0.008	-0.010	7.324	15	-0.022	-0.024	106.67
7	-0.001	-0.004	3.979	16	0.130	0.129	141.67
8	-0.001	-0.004	3.979	17	0.003	0.006	27.30
9	0.129	0.141	141.67	18	-0.197	-0.190	—
				19	-0.197	-0.200	—

given in Table II. In both tables, the shifts in the NMR spectra (δ -units from TMS) are given for each hydrogen and carbon atom.

An analysis of the data revealed that the shifts of the signals of the hydrogen atoms at the furan ring correlate with the INDO charges at the corresponding carbon atoms. This correlation implies that magnetic shielding depends linearly on the electron density near the nucleus. The correlations between the $^1\text{H-NMR}$ shifts and INDO charges are expressed by the following equations:

for the structures *Ia, II*:

$$\delta = 6.397\xi + 6.452, \quad r = 0.9973;$$

TABLE II
INDO Charges and ^{13}C and $^1\text{H-NMR}$ Shifts for 2-Benzylfuran and Diphenylmethane

2-Benzylfuran			Diphenylmethane		
Atom	charge	shift ^a	Atom	charge	shift ^a
1	-0.026	7.232	1	-0.027	7.185
2	-0.028	7.232	2	-0.030	7.185
3	-0.028	7.232	3	-0.032	7.185
4	-0.033	7.232	4	-0.039	7.185
5	0.034	7.232	5	0.108	7.185
6	0.017	5.959	6	-0.027	7.202
7	-0.011	6.262	7	-0.030	7.202
8	-0.020	7.244	8	-0.032	7.202
9	-0.011	3.945	9	-0.039	7.202
10	-0.011	3.945	10	0.108	7.202
11	0.042	138.21	11	-0.018	3.950
12	0.011	128.73	12	-0.018	3.950
13	0.030	128.41	13	0.052	141.15
14	0.019	126.39	14	0.006	128.97
15	0.039	128.41	15	0.034	128.41
16	-0.053	128.73	16	0.015	126.03
17	0.163	154.64	17	0.047	128.41
18	-0.072	110.40	18	-0.134	128.97
19	0.027	106.35	19	0.052	141.15
20	0.135	141.27	20	0.006	128.97
21	0.026	34.29	21	0.034	128.41
22	-0.198	—	22	0.015	126.03
			23	0.047	128.41
			24	-0.134	128.97
			25	0.035	41.87

^a ^1H -shifts of benzene protons were read as the centre of gravity of the multiplet.

for the structures *Ib*, *II*:

$$\delta = 6.358\xi + 6.442, \quad r = 0.9979.$$

For the number of points processed (9), to the critical correlation coefficient at the 99.9% level of significance corresponds the value $r = 0.8982$.

With regard to the fact that the ^{13}C shifts represent a scale of the total electron density in the environment of the pertinent nuclei and generally are not affected by magnetic anisotropy to such an extent as the ^1H shifts, it is surprising that the significance of the ^1H correlations is rather high and that the analogous dependences for the ^{13}C shifts are characterized by correlation coefficients slightly worse, though essentially higher than the critical value for 99.9% for the processed 12 values ($k = 0.8233$). The correlations obtained are characterized by the equations as follows:

$$Ia, II: \delta = 191.597\xi + 117.979, \quad r = 0.9654;$$

$$Ib, II: \delta = 194.010\xi + 117.828, \quad r = 0.9727.$$

Now we compared the theoretically expected probability of anodic attack at the various positions of *III*, expressed *via* the INDO charges at the corresponding carbon atoms, with the experimental data obtained¹ during anodic acetylation of the compound.

Position of <i>III</i>	INDO charge*	anodic attack, %
<i>ortho</i>	-0.064	35.3
<i>para</i>	0.015	37.3
alpha	0.035	18.7
<i>meta</i>	0.041	8.7

Evidently the calculation favours the *ortho* position; this can be explained regarding the fact that the actual transition state cannot be included in the calculation. The attack of the electrochemically generated particle by the acetate anion must involve the *ortho* effect.

It can be summed up stating that a very good agreement was found between experimental properties of the compounds studied and their theoretical values. The INDO method reflects in this case satisfactorily the state within the molecules investigated, particularly within their heterocyclic part.

* For the *ortho* and *para* positions, arithmetic means obtained from the electron charges for the two nonequivalent positions of the benzene ring were used.

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