1,3-Diphenylbenzo[*c*]furan Dianion: Nuclear Magnetic Resonance Characterization of a 4*n*π Heterocyclic Dianion containing Oxygen

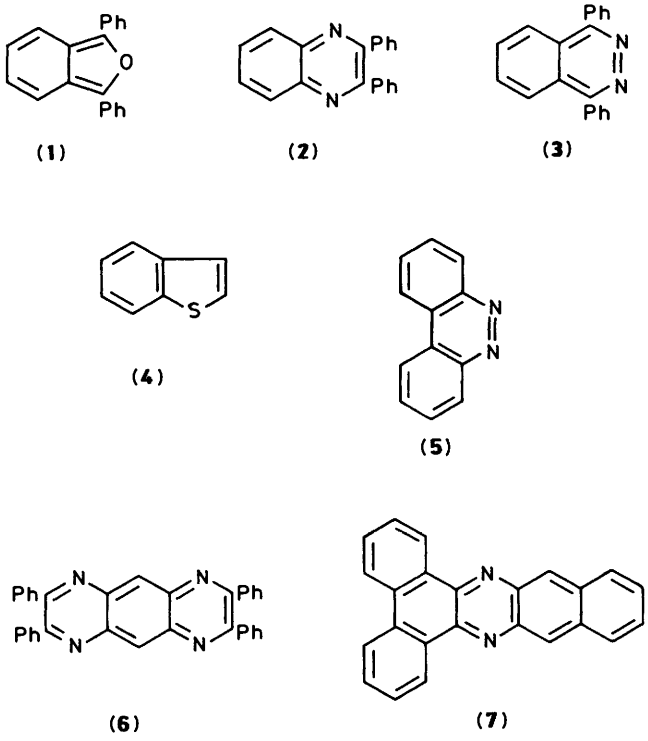
Yoram Cohen, Joseph Klein,* and Mordecai Rabinovitz*
Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

The metal reduction of 1,3-diphenylbenzo[*c*]furan (**1**) to the corresponding dianion ($\mathbf{1}^{2-}$) has been carried out by alkali-metals. A detailed (1D and 2D) n.m.r. investigation of ($\mathbf{1}^{2-}$) enables characterization of its charge distribution as well as its spatial structure. The spectra of ($\mathbf{1}^{2-}$) differs when three alkali-metals are used for the reduction process. These differences are explained by an ion-solvation equilibrium which in turn explains the different stereoselectivity observed in the quenching experiments of the salts of ($\mathbf{1}^{2-}$). The reduction process induces in ($\mathbf{1}^{2-}$) a very high energy barrier for the rotation of the phenyl substituents.

In 1965 Breslow introduced the term antiaromaticity [1] and since then 4*n*π charged systems have been investigated extensively both by spectroscopists and theoretical chemists.[2] These systems are of great interest as they serve as test cases and model compounds in the quest for the notion of aromaticity.[3] Aromatic or antiaromatic systems are defined as systems in which the π-electron delocalization reduces or increases the energy content with respect to a model compound. The application of this criterion is difficult and indices based on theoretical concepts such as Hückel rule,[4] Platt's peripheral model,[5a] and Randić's conjugated circuits [5b] model were suggested. Recently, we were able to demonstrate that the charge alternation concept [6] introduced in the polymetalation reaction of allylic and benzylic systems predicts and rationalizes the charge distribution of conjugated polycyclic dianions.[6b] The neutral carbocyclic derivatives and the charged systems derived from them having a rigid and nearly planar configuration, offer the opportunity of studying the relationships between the electronic structure and the system's properties. Among the experimental techniques which enable characterization of dianions, n.m.r. is the most powerful and to date a host of n.m.r. data is available for such carbocyclic anions.[2,3,7] It should be noted that magnetic anisotropy as deduced from the ^{1}H n.m.r. parameters can serve as a useful index for the estimation of aromaticity (diatropicity) of the system under investigation. In addition, ^{13}C n.m.r. spectra shed light on the charge distribution over the π framework of the system, a parameter which is of major importance in characterizing charged systems.

In view of our interest in the preparation and the spectroscopic characterization of 4*n*π fully conjugated dianions and their relevance to aromaticity, we undertook the investigation of the metal reduction of 1,3-diphenylbenzo[*c*]furan (**1**). Recently, we were able to prepare and characterize by n.m.r. spectroscopy nitrogen and sulphur 4*n*π polycyclic dianions [8,9] [*e.g.* ($\mathbf{2}^{2-}$)—($\mathbf{7}^{2-}$)]. The lack of n.m.r. spectroscopic information concerning oxygen-containing heterocyclic dianions prompted us towards this study. Substrate (**1**) seemed to be the compound of choice for such a study in view of the fair stability of the dianion ($\mathbf{1}^{2-}$) [10] and narrow HOMO – LUMO energy gap calculated for the unsubstituted parent compound, *viz.* benzo[*c*]furan.[11]

We report the first n.m.r. characterization of an oxygen-containing heterocycle of a 4*n*π dianion, *viz.* 1,3-diphenylbenzo[*c*]furan dianion ($\mathbf{1}^{2-}$). A detailed n.m.r. investigation (1D and 2D [12]) afforded a full assignment of the ^{1}H and the ^{13}C n.m.r. spectra of ($\mathbf{1}^{2-}$). These assignments enabled a complete characterization of the alternating charge distribution as well as the spatial structure of ($\mathbf{1}^{2-}$). The dependency of the spectral parameters of ($\mathbf{1}^{2-}$) (^{1}H and ^{13}C n.m.r.) on the alkali-metal used for the reduction will be discussed and the relationship to the stereoselectivity of the quenching experiments of ($\mathbf{1}^{2-}$)[10] will be demonstrated. This dependency is rationalized by a shift of their ion pairing equilibrium. The electron-transfer reaction [*i.e.* (**1**) ⟶ ($\mathbf{1}^{2-}$)] induces hindrance of the free rotation about the carbon–carbon bond of the phenyl substituents as manifested both by the ^{1}H and ^{13}C n.m.r. spectra.



Results

Reduction of (**1**) to the corresponding dianion ($\mathbf{1}^{2-}$) by alkali-metals (Li, Na, K) was carried out in [$^2H_8$]THF at −78 °C. The ^{1}H and ^{13}C n.m.r. parameters of the neutral and the charged systems are reported in Tables 1 and 2. The first step which is a one-electron reduction afforded a green solution which gave no n.m.r. spectrum. A few days later a change in colour occurred and the blue solution afforded well resolved proton and carbon spectra attributed to dianion ($\mathbf{1}^{2-}$). Very sharp lines were obtained only in the case of the ^{1}H n.m.r. spectrum of ($\mathbf{1}^{2-}$)–

Table 1. ^1H and ^{13}C N.m.r. parameters of 1,3-diphenylbenzo[*c*]furan (**1**) and its respective dianion ($\mathbf{1}^{2-}$)

Compound	Solvent (*T*/K)	N.m.r. parameters[a,b]	Centre of gravity of the spectra
(**1**)	THF (294)	^1H:[b] 8.07 (dt, J_1 7.3, J_2 1.1, 2′-,6′-H), 7.98, 7.09 (AA′BB′, 4-,7-H, 5-,6-H), 7.55 (tt, J_1 7.6, J_2 1.0, 3′-,5′-H), 7.35 (tt, J_1 7.4, J_2 1.3, 4′-H)	7.76
		^{13}C:[c] 144.2 (C-1,-3), 132.2 (C-1′), 129.3 (C-3′,-5′), 127.2 (C-4′), 125.6 (C-5,-6), 125.1 (C-2′,-6′), 122.7 (C-3a,-7a), 120.5 (C-4,-7)	128.1
$(\mathbf{1}^{2-})$–$2Na^+$	THF (294)	^1H:[d] 6.68 (t, *J* 7.6, 5′-H), 6.63 (t, *J* 7.6, 3′-H), 6.18 (d, *J* 8.4, 2′-H), 5.92 (d, *J* 8.2, 6′-H), 5.83, 5.73 (AA′BB′, 5-,6-H, 4-,7-H), 5.39 (t, *J* 6.7, 4′-H)	6.05
	THF (223)	^1H: 6.61 (t, *J* 7.3, 5′-H), 6.55 (t, *J* 7.7, 3′-H), 6.09 (d, *J* 8.1, 2′-H), 5.82 (d, *J* 7.4, 6′-H), 5.81, 5.73 (AA′BB′, 5-,6-H, 4-,7-H), 5.23 (t, *J* 6.5, 4′-H)	5.98
	THF (203)	^1H: 6.52 (t, *J* 7.3, 5′-H), 6.45 (t, *J* 7.1, 3′-H), 5.99 (d, *J* 8.2, 2′-H), 5.77 (d, *J* 7.9, 6′-H), 5.75, 5.70 (AA′BB′, 5-,6-H, 4-,7-H), 5.13 (t, *J* 6.6, 4′-H)	5.90
	THF (300)	^{13}C:[c] 133.0 (C-3a,-7a), 129.3 (C-5′), 128.1 (C-3′), 127.7 (C-1′), 116.1 (C-1,-3), 114.1 (C-5,-6), 109.4 (C-2′), 105.9 (C-6′), 101.4 (C-4′), 99.5 (C-4,-7)	116.5
	THF (223)	^{13}C:[c] 133.2 (C-3a,-7a), 129.1 (C-5′), 127.9 (C-3′), 126.6 (C-1′), 116.8 (C-1,-3), 114.0 (C-5,-6), 109.0 (C-2′), 105.4 (C-6′), 100.4 (C-4′), 99.8 (C-4,-7)	116.2
	THF (203)	^{13}C:[c] 133.6 (C-3a,-7a), 128.8 (C-5′), 127.6 (C-3′), 125.9 (C-1′), 117.9 (C-1,-3), 113.9 (C-5-,6), 108.8 (C-2′), 105.8 (C-6′), 101.1 (C-4′), 98.2 (C-4,-7)	116.2
$(\mathbf{1}^{2-})$–$2K^+$	THF (294)	^1H:[e] 6.63 (m, 3′-,5′-H), 6.18 (d, *J* 7.4, 2′-H), 5.95 (d, *J* 6.9, 6′-H), 5.83, 5.78 [AA′BB′(b), 5-,6-H, 4-,7-H], 5.35 (t, *J* 6.5, 4′-H)	6.05
	THF (223)	^1H:[e] 6.57 (m, 3′-,5′-H), 6.12 (d, *J* 8.0, 2′-H), 5.91 (d, *J* 7.7, 6′-H), 5.81, 5.73 [AA′BB′(b), 5-,6-H, 4-,7-H], 5.27 (t, *J* 6.3, 4′-H)	6.00
	THF (223)	^{13}C:[e] 133.5 (C-3a,-7a), 129.2 (C-5′), 127.8 (C-3′), 126.7 (C-1′), 115.1 (C-1,-3), 114.4 (C-5,-6), 109.1 (C-2′), 105.7 (C-6′), 101.3 (C-4′), 99.9 (C-4,-7)	116.3
$(\mathbf{1}^{2-})$–$2Li^+$	THF (294)	^1H:[e] 6.51 (bt, *J* 6.2, 3′-,5′-H), 5.97 (t, *J* 8.6, 2′-,6′-H), 5.75, 5.69 (AA′BB′, 5-,6-H), 5.19 (t, *J* 6.6, 4′-H)	5.94
	THF (223)	^{13}C:[e] 133.9 (C-3a,-7a), 127.3 (C-5′),[f] 127.2 (C-3′),[f] 127.1 (C-1′),[f] 117.4 (C-1,-3), 113.4 (C-5,-6), 107.9 (C-2′),[g] 107.7 (C-6′),[i] 100.5 (C-4′), 98.1 (C-4,-7)	116.1

[a] Chemical shifts are reported on the δ scale (p.p.m.) downfield from Me_4Si and coupling constants are given in Hz. Abbreviations are: s = singlet; d = doublet; t = triplet; dt = double triplet; tt = triple triplet; m = multiplet. For numbering see Figure 2. Some of the spectra are shown in Figure 1. [b] Assignment based on T_1 relaxation time and double-resonance experiments. [c] Assignment based on 2D C–H correlation experiments. [d] Assignment based on 2D NOESY, T_1 and double-resonance experiments. [e] Tentative assignment based on the similarity to the spectra of $(\mathbf{1}^{2-})$–$2Na^+$. [f,g] Assignments can be interchanged.

Table 2. N.m.r. spectral parameters, and calculated and experimental charge density of 1,3-diphenylbenzo[*c*]furan dianion ($\mathbf{1}^{2-}$) as disodium salt

	C-1,-3	O_2	C-3a,-7a	C-4,-7	C-5,-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
δ^1H[a]				5.73	5.83		6.18	6.63	5.39	6.68	5.92
$\delta^{13}C$[a]	116.1		133.0	99.5	114.1	127.7	109.4	128.1	101.4	129.3	105.9
$\Delta\delta^{13}C$[a]	−28.1		+10.3	−21.0	−11.5	−4.5	−15.5	−1.2	−26.8	0.0	−19.2
$\Delta q\pi$[b]	−0.242		+0.089	−0.181	−0.099	−0.039	−0.134	−0.010	−0.231	−0.0	−0.166
$\Delta q\pi$[c]	−0.274	−0.11	−0.069	−0.204	−0.134	−0.059	−0.045	−0.025	−0.067	−0.025	−0.045

[a] Chemical shifts are reported on δ scale downfield from Me_4Si in p.p.m. units. $\Delta\delta^{13}C$ are given in p.p.m. units. [b] Experimental charge density as obtained by $\Delta\delta^{13}C/K_c$. [c] Calculated charge density as obtained by ωβ calculations in which the resonance integral (β) of the C-1–C-1′ and C-3–C-1′ bonds equal to 0.5. It should be noted that interchanging this value to 0.7 predicts more accurately the charge in the phenyl substituents and results in bond lengths which may account for the high energy barrier found for the rotation about these bonds (see text).

$2Na^+$ (see Figure 1). The disodium salt $(\mathbf{1}^{2-})$–$2Na^+$ was found to be much more stable than the respective dipotassium and dilithium salts. At −40 °C the disodium salt of $(\mathbf{1}^{2-})$ could be stored for weeks without any detectable decomposition while the dilithium salt had decomposed completely after a few days. This observation is as expected as it has been found that lithium metal causes cleavage of oxygen heterocycles faster than other alkali-metals.[13] For these very reasons, 2D n.m.r. experiments, which are time-consuming, were carried out only on the disodium derivative. The assignments of the spectra of the lithium and potassium salts of $(\mathbf{1}^{2-})$ could be easily deduced from their similarity to the disodium derivative and decoupling experiments. The assignment of the ^1H and ^{13}C n.m.r. spectra of the neutral system (**1**) and the respective dianion $(\mathbf{1}^{2-})$–$2Na^+$ were carried out by double-resonance experiments, T_1 relaxation time measurements,[14a] and 2D n.m.r. spectroscopy. The 2D NOESY experiment[15a] of $(\mathbf{1}^{2-})$–$2Na^+$ was applied to distinguish between the two non-equivalent *ortho* hydrogens of the phenyl substituents, *viz.* 2′- and 6′-H and the components of the AA′BB′ pattern. Based on the conspicuous cross peaks between the components of the 2D NOESY spectrum we attribute the resonances at δ 6.18 and 5.73 to 2′- and 4-,7-H respectively (Table 1, Figure 2). This assignment is corroborated by T_1 relaxation times as measured by the inversion recovery technique.[14a] The shortest T_1 values were found for 2′- and 4-,7-H (Figure 3) due to the through-space *peri*-interaction between these two groups of protons. After this spatial relationship is solved, a complete assignment of the ^1H n.m.r. spectrum is easily achieved by double-resonance experiments (Table 1). In order to assign the protonated and the quaternary carbon atoms of $(\mathbf{1}^{2-})$–$2Na^+$ (see Figures 4 and 5) two different 2D ^{13}C–^1H correlation experiments[15b] were applied. It is well documented that the best experimental measure of electron density in charged species is the change of the carbon chemical

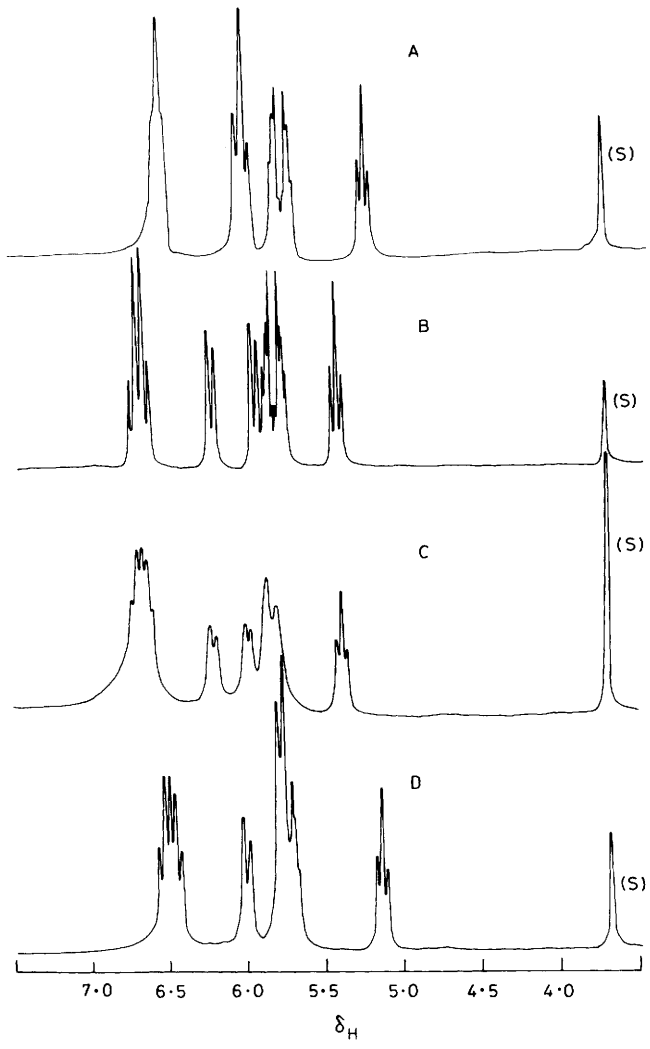


Figure 1. The ^{1}H n.m.r. spectra of 1,3-diphenylbenzo[*c*]furan dianion (1^{2-}) in [$^2H_8$]THF: A, (1^{2-})–2Li$^+$, 291 K; B, (1^{2-})–2Na$^+$, 293 K; C, (1^{2-})–2K$^+$, 294 K; D, (1^{2-})–2Na$^+$, 203 K

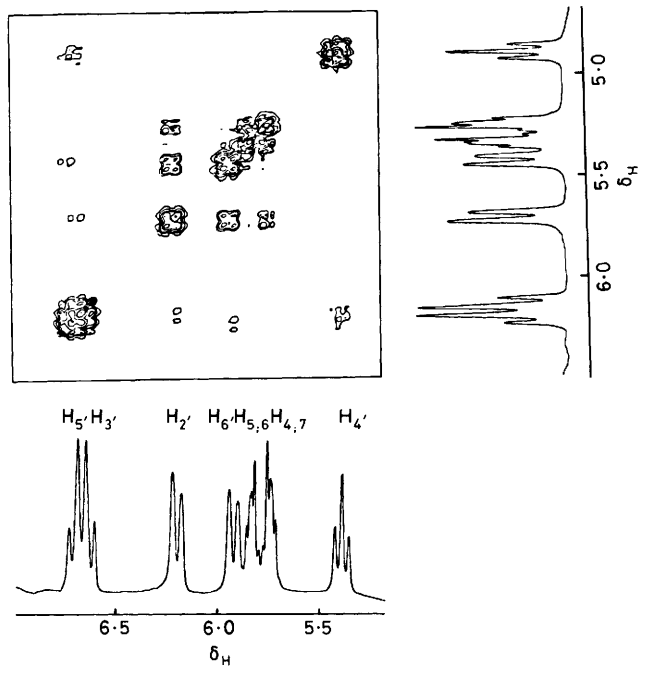


Figure 2. The 2D ^{1}H NOESY spectrum of (1^{2-})–2Na$^+$ in [$^2H_8$]THF at room temperature

shifts at a specific position ([$\Delta\delta^{13}$C], see Table 2). Therefore, efforts were made (including 2D techniques) to assign unambiguously the ^{13}C n.m.r. spectrum of the neutral hydrocarbon (**1**) (see Table 1, Experimental section, and the results shown in Table 2). The dianionic nature of the monitored species was deduced from the ^{1}H and ^{13}C n.m.r. spectra which showed the expected pattern and are shifted to high field, as well as from quenching experiment. The latter gave with dry oxygen the starting material (**1**) as sole product. The calculations were performed by MO-'ωβ' technique amplified by the following parameters for =N–, the aromatic C–N bond, –O– and C–O bond: $\alpha(N) = \alpha(C) + 0.4\ \beta(C\text{–}C)$, $\beta(C\text{–}N) = \beta(C\text{–}C)$, $\beta(N\text{–}N) = \beta(C\text{–}C)$, $\alpha(O) = \alpha(C) + 2\beta(C\text{–}C)$, $\beta(C\text{–}O) = 0.9\ \beta(C\text{–}C)$.[16] In all cases the habitual position used was $\omega = 1.4$.

Discussion

(I) *Charge Delocalization and Paratropicity of* (1^{2-}).—In 1956, Pople revived the interest in the ring current model by relating it to proton chemical shifts.[17] It has been observed that contrary to the diamagnetic (low-field) shifts revealed by $(4n + 2)\pi$ systems, antiaromatic $4n\pi$ systems sustain paramagnetic (high-field) shifts.[18] These high-field shifts were attributed to the term of the shielding constant originating from the mixing of ground and excited states,[14b] which becomes more important in $4n\pi$ systems which are characterized by a low HOMO – LUMO energy gap. Although there were criticisms of the ring current concept[19] and especially of its relationship to aromaticity,[20] it seems that the ^{1}H chemical shift criterion gained wide acceptance as a qualitative measure of the aromatic nature.[19] Benzo[*c*]furan has only a low resonance energy and a narrow HOMO – LUMO gap[11] and thus, despite its $(4n + 2)\pi$ electrons, it cannot be classified as a classical aromatic system. 1,3-Diphenylbenzo[*c*]furan (**1**) has only a moderate thermodynamic stability which may also indicate that it has a limited aromatic character. When a neutral $(4n + 2)\pi$ hydrocarbon has a minor aromatic character, the resulting $4n\pi$ dianion is expected to exhibit negligible paratropicity provided that there are no crucial geometrical changes. The ^{1}H n.m.r. spectra of (1^{2-}) are consistent with this expectation and the AA'BB' pattern attributed to 4-,7-H appears at a relative low field (*i.e.* δ 5.83 and 5.73). Paratropic $4n\pi$ dianions are expected to show pronounced high-field shifts beyond the negative charge effect. In view of the shielding due to the negative charges the absorption of the AA'BB' pattern at δ 5.83 and 5.73 appears at low field indeed. Structurally related heterocyclic dianions such as 2,3-diphenylquinoxaline dianion (2^{2-}) and 1,4-diphenylphthalazine dianion (3^{2-}) were recently investigated.[8b] For comparison, the AA'BB' pattern of the paratropic 2,3-diphenylquinoxaline dianion (2^{2-}) appears at δ 4.67 and 4.13.[8b] In (3^{2-}), the diaza-analogue of (1^{2-}), which was found to exhibit only minor paratropicity, the AA'BB' pattern appears in the same range as that of the AA'BB' pattern of (1^{2-}) (*i.e.* δ 6.33 and 5.84).[8b] The calculated excess of high-field shift (χ_H) is reported in Table 3. This parameter is defined as the difference between the experimental and the calculated centre of gravity of the ^{1}H chemical shifts where only charge effects are taken into consideration. This index was found to be a good quantitative measure of the degree of the paratropicity of carbocyclic dianions.[21] It seems, however, that the values of χ_H cannot serve as a good index for the paratropicity of *heterocyclic* dianions in

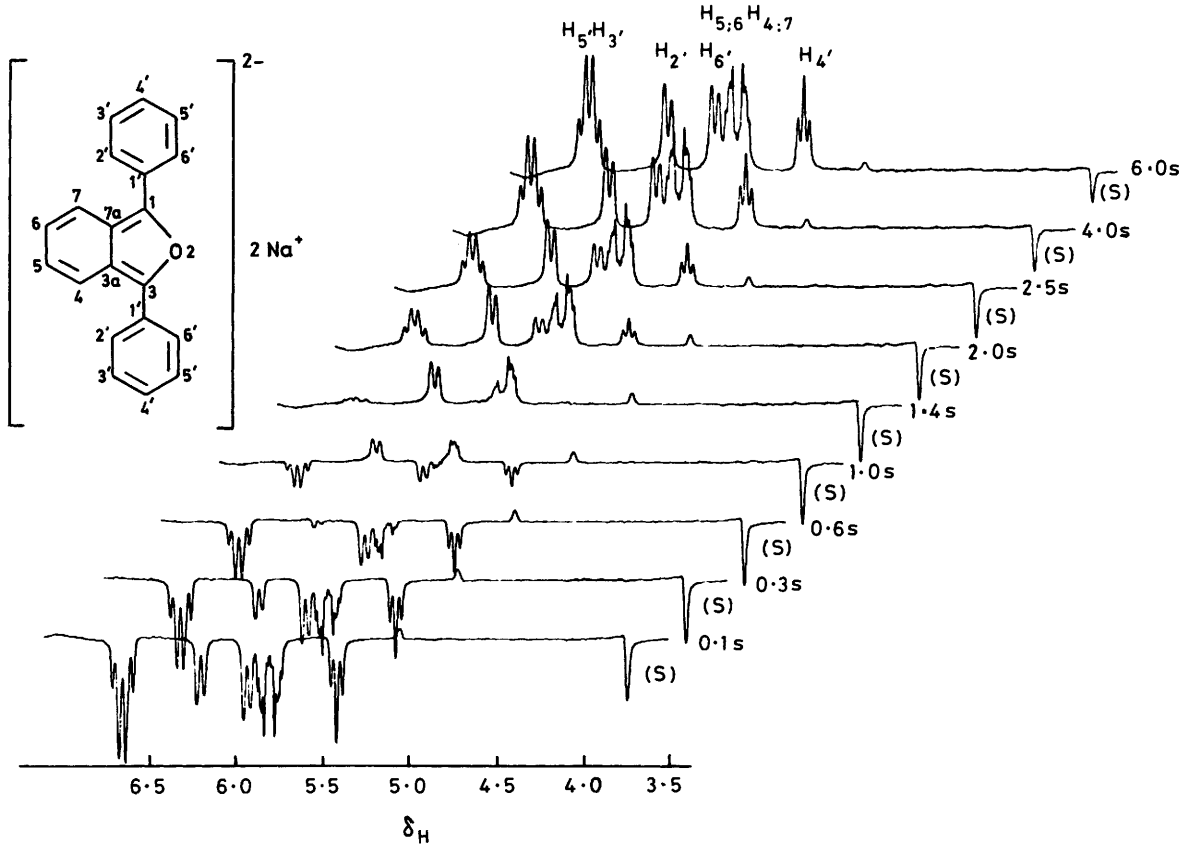


Figure 3. ^{1}H N.m.r. inversion-recovery experiment[14a] of the spectrum of (1^{2-})–2Na$^+$ in [$^2H_8$]THF at room temperature

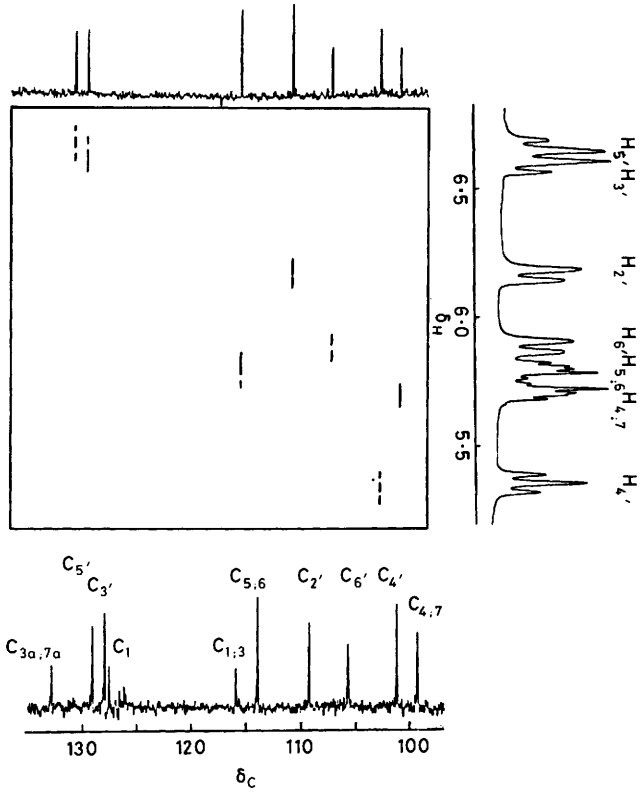


Figure 4. 2D ^{13}C–^{1}H correlation spectroscopy optimized for ^1J(^{13}C,^{1}H) 150 Hz of (1^2)–2Na$^+$ in [$^2H_8$]THF at room temperature

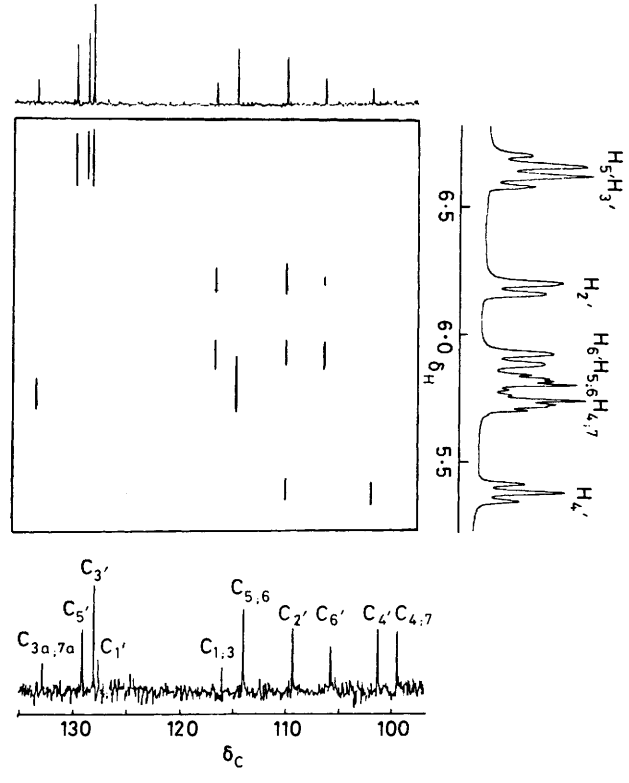
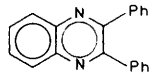
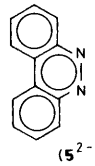
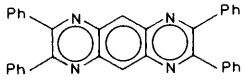
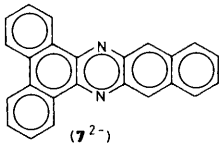
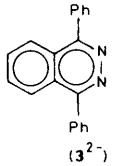
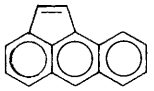
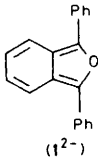


Figure 5. 2D ^{13}C–^{1}H correlation spectroscopy optimized for ^3J-(^{13}C,^{1}H) *ca.* 7 Hz of (1^{2-})–2Na$^+$ in [$^2H_8$]THF at room temperature

Table 3. Dependence of the deviation of the calculated proportionality constants from the experimental ones (ΔK) on the total π charge density on heteroatoms of disodium salts of heterocyclic dianions in [$^2H_8$]THF

Systems	$\Sigma\Delta\delta^{13}C$[a]	χ_H[d]	K_c^{exp}[b]	K_c^{cal}[b,c]	$\Delta K^b = K_c^{cal} - K_c^{exp}$	Total π charge density on heteroatoms
 (2^{2-})	88.0	−0.95	44.0	111.2	67.2	−0.84
 (5^{2-})	43.2	−2.80	21.6	93.7	72.1	−0.68
 (6^{2-})	88.4	−0.67	44.2	109.9	65.7	−1.06
 (7^{2-})	84.0	−1.25	42.0	98.0	56.0	−0.64
 (3^{2-})	198.0	−0.59	99.0	119.8	20.8	−0.41
 (8^{2-})	228.8[e]	−1.13[e]	114.4[e]	112.3[e]	2.1[e]	
 (9^{2-})	225.6	−1.47	112.8	105.8	7.0	
 (1^{2-})	232.4	−0.95	116.2	111.2	5.0	−0.11

[a] The total high-field shift of the ^{13}C spectra is given in p.p.m. [b] The units are p.p.m. per electron. [c] As obtained from equation (1), see also ref. 21(*b*). [d] For details of calculations see text and ref. 22(*b*). [e] Data for the dilithium salt of (8^{2-}).

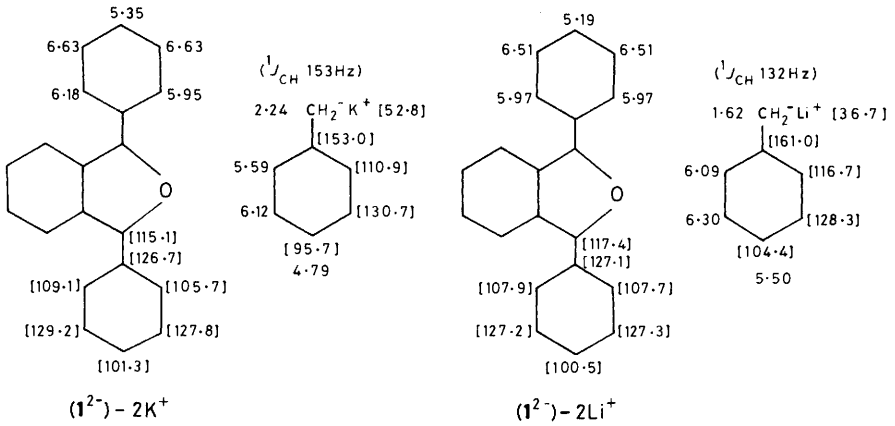
which various numbers and types of heteroatoms occupy different positions. The heteroatoms not bearing a hydrogen atom are the origin of the severe deviations of this parameter, since large amounts of charge can be localized on them. Calculation (ωβ) predicts that only a minor part of the negative charge resides on the oxygen atom of (1^{2-}). The total shift of the carbon spectrum of (1^{2-}) is 232 p.p.m. which corresponds to a proportionality constant (K_c) of 116 p.p.m. per electron (p.p.m./e) (Table 3). This value is within the range found for many carbocyclic dianions.[22] Müllen and Edlund pointed out that the experimental proportionality constant (K_c) varies considerably. It was found that when the anisotropic effect is considered, a correlation can be derived to predict the proportionality constant (K_c^{cal}). Following this approach,[21b] the expected value for (K_c^{cal}) for dianions is given by equation (1) where n_c is the number of carbon atoms in the system.

$$K_c^{cal} = 134 + 1.2\, n_c\chi_H \quad (1)$$

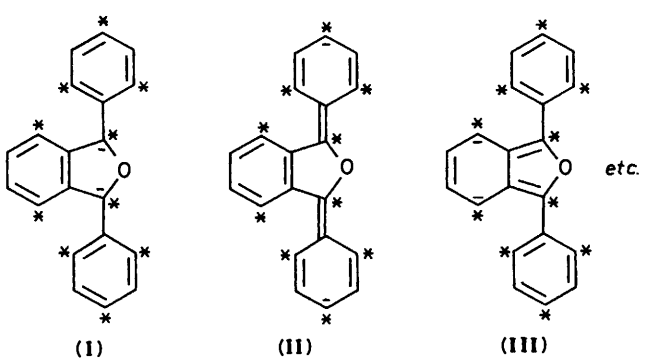
It is expected that in heterocyclic dianions the differences (ΔK) between the calculated values of the proportionality constant (K_c^{cal}) and the experimental one (K_c^{exp}) will be significant (Table 3). The higher the charge density residing on the heteroatoms (nitrogen or oxygen), the larger should be the expected deviation. The results summarized in Table 3 show that this is indeed the case. For the aceanthrylene dianion ($\mathbf{8}^{2-}$) and acephenanthrylene dianion ($\mathbf{9}^{2-}$), the deviations are small (*i.e.* 2.1 and 7.0 p.p.m./e) while in the case of the diaza dianions ($\mathbf{2}^{2-}$) and ($\mathbf{5}^{2-}$)—($\mathbf{7}^{2-}$) the deviations exceed 50 p.p.m./e. It is interesting to note that in the case of 1,4-diphenylphthalazine dianion ($\mathbf{3}^{2-}$) where the calculation predicts only 0.41 units of charge on the two nitrogen atoms, the deviation is only 20 p.p.m./e. The diaza analogue of ($\mathbf{1}^{2-}$), *viz.* ($\mathbf{3}^{2-}$), shows a total carbon shift ($\Sigma\delta^{13}C$) which is considerably higher than the value observed in other diazaheterocyclic dianions. The data of 1,3-diphenylbenzo[*c*]furan dianion ($\mathbf{1}^{2-}$) are even more convincing: (a) $\Sigma\Delta\delta^{13}C$ is 232 p.p.m. which is as high as the values found for many carbocyclic dianions[22] (Table 2); (b) ΔK is very low (only 5.3 p.p.m./e) in line with the small amount of charge which is predicted by calculations to reside on the oxygen (-0.11 units of charge). It should be noted that on going from the neutral system (**1**) to the respective dianion a lowering of the positive charge that resides on the oxygen atom occurs. However, this change in the charge density on the oxygen is not very meaningful as it is small and reflects only the π charge density. The question now arises what is the charge distribution of the system. From the ^{13}C spectra it can be concluded that much of the charge is located at C-1 and -3 and at the *para* positions of the phenyl groups (C-4′). The comparison of the ^1H and ^{13}C chemical shifts of ($\mathbf{1}^{2-}$)–2Li$^+$ and ($\mathbf{1}^{2-}$)–2K$^+$ with those of benzyl-lithium[23] and benzylpotassium[24] is shown in the Scheme. This comparison is instructive and it appears that the absorption bands of the ^1H and ^{13}C n.m.r. spectra of the phenyl substituents in ($\mathbf{1}^{2-}$)–2Li$^+$ are at higher field than those of benzyl-lithium. Based on these observations, ($\mathbf{1}^{2-}$) can be regarded, at first sight, as being composed of two isolated benzyl anions [structure (**I**)].[10]

However, this presentation of ($\mathbf{1}^{2-}$) is not totally accurate as can be seen both from calculated and experimental data ($\Delta\delta^{13}C$, Table 2). These data show that there is a considerable amount of negative charge over the benzo ring (C-4—7) and at the *ortho* and the *para* positions of the phenyl groups (C-4′, -2′, -6′). Therefore, the best representation of ($\mathbf{1}^{2-}$) is the resonance hybrid of structures (I)—(III). The importance of structure (II) is manifested by the high energy barrier for the rotation about C-1–C-1′ and C-3–C-1′ bonds. It should be noted that the charge distribution of ($\mathbf{1}^{2-}$) obeys the rules of the charge alternation concept.[6] The data in Table 2 clearly show that the negative charge is distributed unevenly and resides only on a starred set of carbon atoms in (I)—(III). This pattern of charge distribution results in donor–acceptor interactions which stabilizes the charged system.

(II) *Spatial Structure and Ion Pairing of* 1,3-*Diphenylbenzo*[c]*furan Dianion* ($\mathbf{1}^{2-}$).—From the 2D NOESY spectra it can be concluded that the distance between 4-,7-H and 2′-H is very short indeed. It is probable that C-1 and -3 are pyramidal, as suggested by Smith,[10] particularly in view of their being carbanionic centres α to oxygen.[25] In such a structure the two metal cations will be on the same side of the furan ring. The best spatial presentation of ($\mathbf{1}^{2-}$) seems to be the one in which the oxygen is puckered up in such a way that the phenyl groups adopt pseudoequatorial positions.[10] The similarity between the n.m.r. spectra (^1H and ^{13}C) of the potassium and the sodium salts of ($\mathbf{1}^{2-}$) is evident. Both these spectra differ from the



Scheme.



(I) (II) (III)

spectrum of ($\mathbf{1}^{2-}$)–2Li$^+$. It seems that these differences arise from the fact that in ($\mathbf{1}^{2-}$)–2Na$^+$ and ($\mathbf{1}^{2-}$)–2K$^+$ contact ion pairs dominate while in the case of the small lithium cation the solvent-separated ion pairs prevail. It is accepted that on going from potassium cation to the small lithium cation the ion-solvation equilibrium is shifted towards solvent-separated ion pairs since the energy gained by the solvation process of the small lithium cation exceeds that of the bigger alkali-cations.[26] The comparison with the n.m.r. spectra of benzyl-lithium and benzylpotassium is instructive. These two species are believed to exist in THF as contact ion pairs, and in the case of benzyl-lithium the α-carbon has nearly sp^3 hybridization.[23] Therefore, relative to benzylpotassium, in benzyl-lithium the cation polarizes much of the charge towards the α-carbon atom and

consequently less charge is delocalized into the benzene ring (Scheme). For this reason the *para* carbon of benzylpotassium appears at δ 95.7 p.p.m.[24] while that of the lithio derivative appears at considerably lower field (δ 104.4 p.p.m.).[23] Contrary to these observations, the data for (1^{2-})–$2Li^+$ and (1^{2-})–$2K^+$ show the opposite trend (Scheme). In (1^{2-})–$2Li^+$ more charge is delocalized towards the phenyl substituents and the benzo ring (Scheme). If the Li^+ cation forms contact ion pairs with (1^{2-}) (as in benzyl anion) one would expect an enhanced charge polarization towards C-1 and -3. Therefore, we come to the conclusion that the potassium and sodium cations form contact ion pairs while the small lithium cation shifts the equilibrium toward solvent-separated ion pairs. The solvated lithium cation can polarize less the charge toward the benzylic positions C–1 and C–3 [structure (I)]. This ion-solvation equilibrium explains the pronounced stereoselectivity reported on the alkylation of (1^{2-})–$2Na^+$, (1^{2-})–$2K^+$ *versus* the lower stereoselectivity observed in (1^{2-})–$2Li^+$.[10] As the metal cation is removed from the carbanionic centre, the chance of this centre becoming planar is enhanced, thus rendering the reaction less stereoselective. On these grounds it is expected that (1^{2-})–$2Li^+$, in which the cation is remote from the carbanionic centre, will undergo a less stereoselective alkylation reaction. This was indeed observed in the alkylation of 1,3-diphenylbenzo[*c*]furan dianion[10] (1^{2-}). The stereoselectivity of the sodium and the potassium salts of (1^{2-}) is nearly the same. The similarity of their spectra (Figure 1) predicts a similarity of their ion-solvation state, which may account for this observation.

While the differences between the *ortho* hydrogens (2′-,6′-H) and carbons (C-2′,-6′) of the phenyl substituents of the sodium and potassium salts of (1^{2-}) are significant, the lithium derivative, *i.e.* (1^{2-})–$2Li^+$, shows a much less pronounced effect (Table 1, Figure 1). It seems that this observation may be partially caused by the shielding effects of the alkali-cation. In the case of the dilithium salt of (1^{2-}) a much higher degree of solvent-separated ion pairing may exist and consequently reducing the influence of the anisotropic effects of the alkali-metal.

It has been found that in the course of charging geometrical and conformational changes may occur. Recently, a dynamic process was observed in substituted benzocyclo-octatetraene dianions.[27] The two-electron reduction process which forms (1^{2-}) induces a hindrance of the free rotation of the phenyl groups, as concluded from the ^1H and ^{13}C n.m.r. spectra (Figure 1, Table 1). The flow of charge into the phenyl groups may increase the bond order of the C-1–C-1′, and C-3–C-1′ bonds, thus increasing the energy barrier of the rotation about these bonds. Interestingly, the energy barrier of the rotation is high enough to avoid fast exchange between these sites even at 313 K (200 MHz). The immediate conclusion from these observations is that the suggested structure (II) is indeed a very dominant one.

In view of all the above, it seems that the charge distribution in (1^{2-}) is best represented by the resonance hybrid of structures (I)—(III) as predicted by the charge alternation concept.[6]

Experimental

General Procedure for Metal Reduction Process.—Lithium or sodium wire or potassium chips were introduced to the upper part of an extended n.m.r. tube containing the solution (*ca.* 10^{-2}M) of 1,3-diphenylbenzo[*c*]furan (Aldrich) in [$^2H_8$]THF (Aldrich). The solution was frozen, degassed, and the tube was sealed under vacuum. The solutions were brought to contact with the appropriate metal by turning the tube upside down. The reduction was carried out at −78 °C.

Quenching Experiments.—A solution of (1^{2-})–$2Na^+$ was quenched by dry oxygen *via* a syringe at a slow rate at −78 °C. The deep colour disappeared and the ^1H n.m.r. spectrum of the starting material (1) as sole product was obtained.

N.m.r. Measurements.—The n.m.r. spectra were obtained on a Bruker SY-200 Fourier transform spectrometer equipped with a pulse programmer operating at 200.133 and 50.32 MHz for ^1H and ^{13}C n.m.r., respectively. Field/frequency regulations were maintained by ^2H locking. The free induction decay signals were digitized and accumulated on an Aspect-2000 computer.

Two-dimensional n.m.r. experiments. Acquisitions and processing parameters of two-dimensional experiments. (i) Standard homonuclear 2D ^1H–^1H correlation through dipolar coupling experiment (NOESY-90) was performed on (1^{2-})–$2Na^+$. Pulse sequence: D_1–90°x–t_1–90°x–D9–90°x–t_2 = acquisition with D_1 = 2.5 s, t_1 was incremented from 3 μs to 177.72 ms in 64 steps of 2.777 ms and D9 = 0.9 s. The 90°x ^1H pulse was of 8.3 μs and SI2 = TD = 256w, SW2 = 360 Hz, SW1 = ±180 Hz, TD1 = 64w, SI1 = 128w, NS = 16, and DS = 4 acquired for each value of t_1. Total acquisition time was 1 h 26 min. The resulting data matrix was multiplied by sine-bell function yielding, after double Fourier transformation, a 16 K points matrix. After symmetrization, the data were displayed in a contour level plot (Figure 2).

(ii) Heteronuclear ^{13}C–^1H correlation experiments, optimized for $^1J_{CH}$, 150 Hz, were carried out for (1) and (1^{2-})–$2Na^+$.

Pulse sequence. D_1–90°x (^1H)–$t_{\frac{1}{2}}$–180°x (^{13}C)–$t_{\frac{1}{2}}$–D_3–90°y(^1H); 90°x(^{13}C)–D_4–t_2 = acquisition with broad-band ^1H decoupling. The parameters used for (1) were as follows: D1 = 3.0 s, 90°x(^1H) = 17.5 μs (decoupler coil), 90x(^{13}C) and 180x(^{13}C) 7.8 and 15.6 μs, respectively. D_3 = D_4 = 3.3 ms, $t_{\frac{1}{2}}$ was incremented from 3 μs to 61.536 ms by 32 steps of 1.923 ms, SI2 = TD = 2K, SW2 = 1 400, 6 Hz, TD1 = 32w, SI1 = 64w, SW1 = ±130 Hz. For each value of $t_{\frac{1}{2}}$ we acquired NS = 16 and DS = 2 thus resulting in a total acquisition time of 38 min. The resulting data matrix was multiplied by sine-bell function yielding, after double Fourier transformation, a 64 K points matrix which was displayed in contour level plot. For the assignment of the quaternary carbons of (1), we used the same pulse sequence now optimized for J_{CH} 7 Hz which is the upper limit of $^3J_{CH}$.[28] The new parameters were D3 = 0.07 and D_4 = 0.035 s and NS = 64 which result in a total acquisition time of 2 h 18 min (Table 1).

The acquisition parameters for (1^{2-})–$2Na^+$ were as follows: D1 = 3.0 s, 90x(^1H) = 17.5 μs (decoupler coil), 90x(^{13}C) and 180x(^{13}C) 7.8 and 15.6 μs, respectively. D_3 = D_4 = 3.3 ms, $t_{\frac{1}{2}}$ was incremented from 3 μs to 99.968 ms by 64 steps of 1.562 ms, SI2 = TD = 2K, SW2 = 1 923 Hz, TD1 = 64w, SI1 = 128w, SW1 = ±160 Hz, NS = 160, and DS = 4 acquired for each value of t_1 resulting in a total acquisition time of 8 h 45 min. The resulting data matrix was multiplied by sine-bell function yielding, after double Fourier transformation, a 128 K points matrix which was displayed in contour level plot (Figure 4). The assignment of the quaternary carbons of (1^{2-})–$2Na^+$ was carried out using the same technique by interchanging the respective parameters to the following: D3 = 0.07 s, D4 = 0.035 s, $t_{\frac{1}{2}}$ was incremented from 3 μs to 49.984 ms by 32 steps of 1.562 ms, TD1 = 32w, SI1 = 64, NS = 320, DS = 2 resulting in a total acquisition time of 10 h 31 min (Figure 5).

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References

1 R. Breslow, *Chem. Eng. News*, 1965, **43**, 70; *Acc. Chem. Res.*, 1973, **6**, 393.

2 (*a*) T. J. Katz, *J. Am. Chem. Soc.*, 1960, **82**, 3784; (*b*) R. G. Lawler and C. V. Ristago, *ibid.*, 1969, **91**,1534; (*c*) J. F. M. Oth, H. Baumann, J.-M. Gilles, and G. Schröder, *ibid.*, 1972, **94**, 3498; (*d*) R. M. McQuilkin, P. J. Garratt, and F. Sondheimer, *ibid.*, 1970, **92**, 6682; (*e*) K. Müllen, *Helv. Chim. Acta*, 1976, **59**, 1357; *ibid.*, 1978, **61**, 1296; (*f*) A. Minsky, A. Y. Meyer, R. Poupko, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1983, **105**, 5351; (*g*) K. Müllen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *ibid.*, 1982, **104**, 5403; (*h*) A. Minsky and M. Rabinovitz, *ibid.*, 1984, **106**, 6755; (*i*) H. Vogler, *Chem. Scr.*, 1984, **24**, 188; (*j*) C. Glidewell and D. Lloyd, *ibid.*, 1986, **26**, 373; (*k*) H. Vogler, *Tetrahedron*, 1985, **41**, 5383; (*l*) H. Vogler, *Croat. Chem. Acta*, 1984, **57**, 1177.

3 For selected reviews see (*a*) R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsh.*, 1970—1971, **16**, 103; (*b*) R. N. Young, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1978, **12**, 261; (*c*) M. Rabinovitz, I. Willner, and A. Minsky, *Acc. Chem. Res.*, 1983, **16**, 298; (*d*) K. Müllen, *Chem. Rev.*, 1984, **84**, 603.

4 E. Hückel, *Z. Phys.*, 1931, **70**, 204.

5 (*a*) J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484; (*b*) M. Randić, *Chem. Lett.*, 1976, 68; *J. Am. Chem. Soc.*, 1977, **99**, 444.

6 (*a*) J. Klein, *Tetrahedron*, 1983, **39**, 2733; (*b*) Y. Cohen, M. Rabinovitz, and J. Klein, submitted for publication.

7 (*a*) J. F. M. Oth, E. P. Woo, and F. Sondheimer, *J. Am. Chem. Soc.*, 1973, **95**, 7337; (*b*) P. J. Garratt, N. E. Rowland, and F. Sondheimer, *Tetrahedron*, 1971, **27**, 3157; (*c*) R. H. Mitchell, C. E. Klopfenstein, and V. Boekelheide, *J. Am. Chem. Soc.*, 1969, **91**, 4931; (*d*) W. Huber, K. Müllen, and O. Wennerström, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 624; (*e*) B. C. Becker, W. Huber, and K. Müllen, *J. Am. Chem. Soc.*, 1980, **102**, 7803; (*f*) A. Minsky, A. Y. Meyer, K. Hafner, and M. Rabinovitz, *ibid.*, 1983, **105**, 3975; (*g*) B. Eliasson and U. Edlund, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1837; (*h*) K. Müllen, W. Huber, T. Meul, M. Nakagawa, and M. Iyoda, *J. Am. Chem. Soc.*, 1982, **104**, 5403.

8 (*a*) A. Minsky, Y. Cohen, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1985, **107**, 1501; (*b*) Y. Cohen, A. Y. Meyer, and M. Rabinovitz, *ibid.*, 1986, **108**, 7039.

9 Y. Cohen, J. Klein, and M. Rabinovitz, *J. Chem. Soc., Chem. Commun.*, 1985, 1071.

10 J. G. Smith and R. B. McCall, *J. Org. Chem.*, 1980, **45**, 3982.

11 M. H. Palmer and S. M. F. Kennedy, *J. Chem. Soc., Perkin Trans. 2*, 1976, 81.

12 For recent reviews see (*a*) R. Benn and H. Günther, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 350; (*b*) D. L. Turner, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1985, **17**, 281.

13 V. Kalyanaraman and M. V. George, *J. Organomet. Chem.*, 1973, **47**, 225.

14 H. Günther, 'NMR Spectroscopy,' Wiley, Chichester, 1980 (*a*) p. 225; (*b*) p. 365.

15 (*a*) B. H. Meier and R. R. Ernst, *J. Am. Chem. Soc.*, 1979, **101**, 6441; (*b*) A. A. Maudsley and R. R. Ernst, *Chem. Phys. Lett.*, 1977, **50**, 368.

16 Modified ωβ calculations on Coulomb integrals: (*a*) J. A. Berson, E. M. Evleth, Jr., and S. L. Mannatt, *J. Am. Chem. Soc.*, 1965, **87**, 2901; (*b*) G. V. Boyd and N. Singer, *Tetrahedron*, 1966, **22**, 3383; (*c*) A. J. Wohl, *ibid.*, 1968, **24**, 2889.

17 J. A. Pople, *J. Chem. Phys.*, 1956, **24**, 1111.

18 J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, 1966, **88**, 4811.

19 For comprehensive discussion of the ring current theories in n.m.r. see C. W. Haigh and R. B. Mallion, *Prog. Nucl. Magn. Reson.*, 1978, **13**, 303 and references cited therein.

20 R. B. Mallion, *Pure Appl. Chem.*, 1980, **52**, 1541.

21 (*a*) A. Minsky, A. Y. Meyer, and M. Rabinovitz, *Tetrahedron*, 1985, **41**, 785; (*b*) B. Eliasson, U. Edlund, and K. Müllen, *J. Chem. Soc., Perkin Trans. 2*, 1986, 937.

22 Y. Cohen, N. H. Roelofs, G. Reinhardt, L. T. Scott, and M. Rabinovitz, *J. Org. Chem.*, 1987, **52**, 4207.

23 L. D. McKeever and R. Waack, *J. Organomet. Chem.*, 1971, **28**, 145.

24 (*a*) K. Takahashi, M. Takaki, and R. Asami, *Org. Magn. Reson.*, 1971, **3**, 539; (*b*) K. Takahashi, Y. Kondo, and R. Asami, *ibid.*, 1974, **6**, 580.

25 W. C. Still and C. Sreekumar, *J. Am. Chem. Soc.*, 1980, **102**, 1201.

26 (*a*) J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Am. Chem. Soc.*, 1972, **94**, 2306; (*b*) D. H. O'Brien, C. R. Russel, and A. J. Hart, *ibid.*, 1979, **101**, 633; (*c*) T. E. Hogen-Esch, *Adv. Phys. Org. Chem.*, 1977, **15**, 153.

27 W. Heinz, P. Lagensee, and K. Müllen, *J. Chem. Soc., Chem. Commun.*, 1986, 947.

28 A. Bax, J. A. Ferretti, N. Nashed, and D. M. Jerina, *J. Org. Chem.*, 1985, **50**, 3029.

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