On the Nature of Charge Distribution in the 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Dianion. ^{13}C N.M.R. *vs.* Stability Data

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Whereas the ^{13}C n.m.r. spectrum of the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one dianion (**1**) displayed a number of features suggestive of long range π-interactions, its stability was found to be only slightly higher than that of its 6,7-dihydro analogue (**4**) thereby ruling out the possibility that homoaromaticity plays an important role in the stabilization of this species.

Some years ago we examined the nature of charge distribution in the dianion (**1**) by comparing its ^{1}H n.m.r. spectrum with that of its parent ketone, 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (**2**).[1] On the basis of a number of observations, including a sizable upfield shift of 6- and 7-H, it was concluded that the dianion (**1**) was a homoaromatic species as represented by structure (**3**). Because of a number of more recent reports of theoretical[2] and experimental[3] nature that have criticized homoaromaticity in carbanions, we have re-examined the nature of the dianion (**1**), and herewith report our findings. Our experiments show that whereas a comparison of the ^{13}C n.m.r. spectrum of (**1**) with that of its parent ketone (**2**) and especially with that of its 6,7-dihydro analogue (**4**) reveals a number of chemical shift changes suggestive of long range π-interactions, the difference in stability between dianions (**1**) and (**4**) is only 0.97 kcal mol^{-1} (cal = 4.184 J), leading to the conclusion that such interactions, if present, impart little, if any, homoaromatic stabilization to the dianion (**1**).

The dianions (**1**) and (**4**) were prepared by a method similar to that described earlier,[1]† and their ^{13}C chemical shifts

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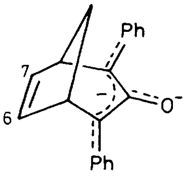
† The dianions (**1**) and (**4**) were prepared in [$^2H_8$]THF–hexane (0.45 M solutions) by sequential treatment of the corresponding ketones (**2**) and (**5**) with KH and Bu^{n}Li.

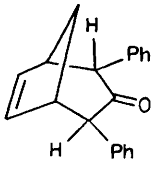
Table 1. ^{13}C Chemical shifts, δ, for the dianions (**1**) and (**4**) and the parent ketones (**2**) and (**5**).

	Carbon atom								
Compound	1(5)	2(4)	3	6(7)	8	ipso	*ortho*	*meta*	*para*
(**1**)	44.8	87.7	164.9	122.8	41.5	146.0	119.3	128.6	110.5
(**2**)[a]	48.6	61.9	206.2	136.3	45.9	139.7	128.6	130.4	127.0
(**4**)	40.6	97.6	169.2	35.2	39.2	144.8	118.1	129.5	109.0
(**5**)[a]	44.9	62.8	205.7	26.5	42.1	139.9	128.5	130.5	126.9

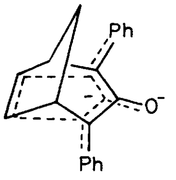
[a] Solvent THF–hexane.



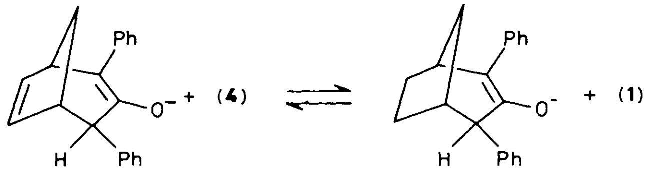
(**1**)



(**2**)

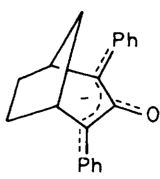


(**3**)

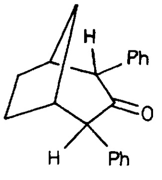


(**6**) (**7**)

Scheme 1



(**4**)



(**5**)

together with those of their parent ketones (**2**) and (**5**) are shown in Table 1. The vinylic carbons C-6 and C-7 of the dianion (**1**) have undergone a 13.5 p.p.m. upfield shift relative to their counterparts in the parent ketone (**2**). Interestingly, C-6 and C-7 in (**3**), the saturated dianion, displayed a *downfield* shift of 8.73 p.p.m. relative to its parent ketone (**5**). Although the origin of this difference is not clear, its presence nonetheless augments the significance of the upfield shift displayed by the vinylic carbons C-6 and C-7 in the dianion (**1**). In the past, such upfield shifts have been attributed to long range π-interactions,[1,4] although more recent studies have questioned these conclusions.[3] A second point of interest comes to light when the chemical shifts of C-2 and C-4 of the dianions (**1**) and (**4**) are compared (Table 1). Thus, although C-2 and C-4 in both dianions have undergone downfield shifts relative to their parent ketones,‡ it can be seen that the unsaturated dianion (**1**) underwent a considerably smaller downfield shift than its saturated analogue (**4**) (25.8 *vs.* 34.8 p.p.m.). In the absence of other evidence to the contrary, this difference could be attributed to a higher sp^3 character of C-2 and C-4 in the unsaturated dianion (**1**) resulting from partial bonding of these carbons with C-6 and C-7 of the vinylic bridge. Finally, the 4.3 p.p.m. upfield shift of the carbonyl carbon, C-3, in the unsaturated dianion (**1**) relative to its counterpart in (**4**) could likewise be explained on the basis of long range π-interactions as depicted in (**3**).

In order to examine the extent to which homoaromatic delocalization may contribute to the stabilization of the dianion (**1**), a method was developed by which the stability of this intermediate relative to that of its saturated analogue (**4**) could be evaluated. The method involved the direct measurement of the equilibrium constant, *K*, for the reaction in Scheme 1 using ^{13}C n.m.r. spectroscopy.[5]

The value of *K* represents the difference in acid strengths of the enolate monoanions (**6**) and (**7**), and is equal to the difference in pK_a values between these two carbon acids.[6] The experiment was carried out by treating an equimolar mixture of the monoanions (**6**) and (**7**) with 1 mol. equiv. of n-butyl-lithium followed by equilibration at room temperature. In a typical experiment, 1.8 mmol each of ketones (**2**) and (**5**) were converted into their enolate monoanions (**6**) and (**7**) by treatment with potassium hydride in tetrahydrofuran (THF)–[$^2H_8$]tetrahydrofuran, and the resulting clear solution was subsequently treated with n-butyl-lithium (1.8 mmol) to give the species in Scheme 1. The mixture was allowed to equilibrate for 48 h at room temperature, and its ^{13}C n.m.r. spectrum was recorded under conditions suitable for quantitative measurements.§ The value of *K* was determined on the basis of the peak areas of the C-2 and -4 resonances of the dianions (**1**) and (**4**) appearing at δ 87.7 and 97.6, respectively[5] (Table 1). From these measurements ΔpK_a for the monoanions (**6**) and (**7**) was found to be 0.71, corresponding to a difference in stabilization energy between the dianions (**1**) and (**4**) of *ca.* 0.97 kcal mol^{-1}. These differences are well within the range expected for an isolated, noninteracting, carbon–

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‡ The downfield shift of carbons C-2 and C-4 in the dianions (**1**) and (**4**) is the net result of two opposing factors, namely, the introduction of the negative charge and the rehybridization of these two positions from sp^3 to sp^2 (J. B. Lambert and S. M. Wharry, *J. Am. Chem. Soc.*, 1982, **104**, 5857; H. O. House and W. V. Prabhu, *J. Org. Chem.*, 1976, **41**, 1209).

§ Spectra were recorded using a Bruker WH-300 spectrometer equipped with an ASPECT 2000 computer. A delay time of 6 s was used, and differential nuclear Overhauser enhancement was eliminated by making use of the gated decoupling technique (A. E. Derome, 'Modern N.M.R. Techniques for Chemistry Research,' Pergamon Press, Oxford, 1987, pp. 112—114; R. J. Abraham and P. Loftus, 'Proton and Carbon-13 N.M.R. Spectroscopy,' Heyden, Bristol, 1978, pp. 150—158); a delay time of 10 s did not change the ratio of the peak areas under consideration. In a separate experiment an equimolar mixture of the dianions (**1**) and (**4**) was prepared and its ^{13}C n.m.r. spectrum recorded under the above conditions. The ratio of the peak areas of the C-2 and -4 resonances the two dianions was found to be 1 : 1.

carbon double bond,[7] and lead to the conclusion that the dianion (**1**) receives little, if any, stabilization through homoaromatic delocalization.

It is not clear at this point what may be the origin of the differences in chemical shifts between dianion (**1**) and its saturated analogue (**4**) or for that matter its parent ketone (**2**). It has been suggested that weak, long-range π-interactions need not necessarily lead to significant extra stabilization of the anion.[8] Whether this situation applies to the dianion (**1**) must await further study. The method developed for measuring ΔpK_a between carbon acids (**6**) and (**7**) provides a simple and straightforward procedure for the determination of the second ionization constants of ketones and related systems.

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