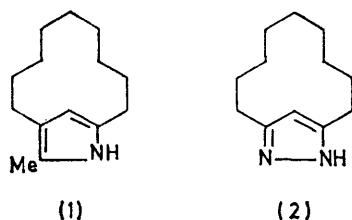


displacement of certain bridge methylene(s) owing to aromatic ring-current effects. In the corresponding



anions (Table I) the signals of these methylenes are not appreciably affected, thus proving that, within the limits of sensitivity of the method, there is no appreciable variation of ring-current effects and hence of aromaticity. Contribution (i) can therefore be neglected.

aprotic solvent and (2) that anisotropies of hetero-atom(s) are nearly constant in the two species, $\Delta\nu$ values for a given position in the heterocycle (Table I) should reflect to some extent the variation of π -electron density on the carbon at that position. On this basis tabulated results suggest that electron density is greater at every position in each aza-anion than in the corresponding neutral precursor. The soundness of this conclusion supports *a posteriori* the hypothesis that terms (ii) and (iii) are relatively unimportant for a qualitative speculation.

It is also found that the values of $\Delta\nu$ for analogous positions in different aza-anions increase with increasing aza-substitution, that is, with the acidity of the precursors. The trend, though not linear suggests that, moving from a π excess (pyrrole) to a highly deficient

TABLE I

¹H N.m.r. data for anions of five-membered aza-heterocycles ^a

Compound	Solvent	Cation	2	3	4	5
Pyrrole	DMSO	Na	3.50 (0.23)	4.28 (0.31)	4.28 (0.31)	3.50 (0.23)
2,4-Dimethylpyrrole	DMSO	Na	7.93 (0.05)	4.73 (0.26)	8.05 (0.00)	3.97 (0.26)
5-Methyl-2,4-nonamethylenepyrrole (1) ^{b,c}	DMSO	Na		4.58 (0.20)		7.95 (0.07)
Imidazole	DMSO	Na	2.88 (0.44)		3.31 (0.38)	3.31 (0.38)
2-Methylimidazole	DMSO	Na	7.83 (0.05)		3.46 (0.31)	3.46 (0.31)
Pyrazole	DMSO	Na		2.63 (0.25)	4.07 (0.34)	2.63 (0.25)
3-Methylpyrazole	DMSO	Na		7.83 (0.05)	4.36 (0.36)	2.78 (0.20)
3,5-Dimethylpyrazole	DMSO	Na		7.94 (0.05)	4.68 (0.35)	7.94 (0.05)
3,5-Nonamethylenepyrazole (2) ^{d,e}	DMSO	Na			4.38 (0.35)	
1,2,3-Triazole ^f	DMSO	Na			2.79 (0.59)	2.79 (0.59)
1,3,4-Triazole	DMSO	Na	2.28 (0.63)			2.28 (0.63)
	MeOH	Na	2.06 (0.29)			2.06 (0.29)
	MeOH	Li	2.08 (0.31)			2.08 (0.31)
	MeOH	K	2.04 (0.27)			2.04 (0.27)
Tetrazole	DMSO	Na				1.80 (1.27)
	MeOH	Na				1.57 (0.78)
	MeOH	Li				1.58 (0.79)
	MeOH	K				1.55 (0.76)

^a Chemical shifts are given in τ units (± 0.02 p.p.m.) relative to Me_4Si as internal reference for *ca.* 1M solutions if not otherwise stated; figures in parentheses refer to chemical shift differences (Δ) of the anions relative to their corresponding precursors. ^b *Ca.* 0.5M. ^c Central shielded methylenes 9.63 (0.00). ^d *Ca.* 0.25M. ^e Central shielded methylenes 9.40 (0.08) at 60 °C. ^f *Ca.* 0.35M.

TABLE 2

¹H N.m.r. data (in DMSO) for sodium salts of benzo condensed five-membered aza-heterocycles ^a

Compound	2	3	4	7	5	6
Indole	2.72 (0.03)	3.91 (0.34)	2.70 (0.10)		3.47 (0.50)	
2-Methylindole	7.60 (0.14)	4.17 (0.48)	2.80—3.05 (0.45)		3.35—3.70 (0.70)	
3-Methylindole	2.94 (0.26)	<i>b</i>	2.70—2.90 (0.48)		3.38—3.58 (0.70)	
5-Methylindole	2.86 (0.02)	4.08 (0.34)	3.00 (0.15)		<i>b</i> 3.67 (0.49)	
7-Methylindole	2.85 (0.05)	3.98 (0.28)	2.95 (0.28) <i>b</i>		3.55—3.80 (0.50)	
2,5-Dimethylindole	7.73 (0.05)	4.34 (0.30)	3.19 (0.27) 3.06 (0.12)		7.73 (0.05) 3.75 (0.49)	
Benzimidazole	2.20 (0.47)		2.30—2.65 (0.07)		3.00—3.35 (0.40)	
2-Methylbenzimidazole			2.65—2.90 (0.25)		3.20—3.50 (0.27)	
5,6-Dimethylbenzimidazole	2.47 (0.50)		2.86 (0.17)		7.75 (0.05)	
Indazole		2.18 (0.30)	2.56 (0.26)	2.56 (0.09)	3.48 (0.52)	3.23 (0.53)
5-Chloroindazole		2.08 (0.21)	2.47 (0.32)	2.34 (0.16)		3.21 (0.58)
Benzotriazole			1.85—2.20 (0.00)		2.65—3.00 (0.30)	
5-Methylbenzotriazole			2.52 (0.22)	2.38 (0.26)	<i>b</i> 3.20 (0.47)	

^a Chemical shifts are given in τ units (± 0.02 p.p.m.) relative to Me_4Si as internal reference for *ca.* 1M solutions; figures in parentheses refer to chemical shift differences (Δ) of the anions relative to their corresponding neutral precursors; figures in parentheses in italics refer to the average chemical shift differences. ^b Covered by solvent.

Lack of information about contributions (ii) and (iii) prevent correlation of calculated π -electron density and observed displacements. However, assuming (I) that no dramatic change of solvation occurs between an anion and its neutral precursor in the same dipolar

system (tetrazole), the difference of electron density on the cyclic framework between a nitranion and its neutral precursor increases on increasing the electron deficiency of the latter. Further support for this is given by the consistent decrease of $\Delta\nu$ values due to the

5- and 6-protons (*para* to the nitrogen and to atom 3 in the heterocycle respectively) in anions of indole, benzimidazole, indazole, and benzotriazole. Clearly in benzotriazolyl anion there is less residual electron availability to be displaced on the benzene ring than in indolyl anion.

pK_a Values of 1,2,3-triazole, 1,2,4-triazole, and tetrazole are low enough (9.4, 10.3, and 4.9,¹⁶ respectively) for the corresponding anions to be observed in methanol and water. $\Delta\nu$ Values found in methanol are considerably lower than in dimethyl sulphoxide and chemical shifts of the anions in this solvent are to lower field than in dimethyl sulphoxide. Since, for neutral substrates, specific solvent interactions appear to be similar in the

intimate and solvent-separated ion-pairs are present at the same time. Since no spectra of pure intimate ion-pairs or of pure covalent species are known, minor amounts of covalent species (A) might possibly contribute as well to the equilibria; nothing however can be firmly stated about the position of the equilibria. It has been recently proposed²⁰ that in tetrahydrofuran indolyl-lithium should be regarded as a predominantly solvent-separated ionic species, while sodium and potassium salts should be contact ion-pairs. This proposal was based on very small and intriguing differences of chemical shifts between the alkali-metal salts of indole (which should actually be regarded as mixtures of intimate and solvent-separated ion pairs) and on similar results obtained for

TABLE 3
¹H N.m.r. data for indolyl salts ^a

Run	Solvent	Cation	2	Δ_{mn}^b	3	Δ_{mn}	4	7	5	6	
1	DMSO		2.69		3.58						
2		Na	2.72	$\Delta_{12} = +0.03$	3.91	$\Delta_{12} = 0.33$		2.70	2.77	3.02	
3		Na c.c. ^c	2.74	$\Delta_{13} = +0.05$ $\Delta_{23} = +0.02$	3.93	$\Delta_{13} = 0.35$ $\Delta_{23} = 0.02$		2.72			3.47 3.49
4		Li	2.70	$\Delta_{14} = +0.01$ $\Delta_{24} = -0.02$	3.87	$\Delta_{14} = 0.29$ $\Delta_{24} = -0.06$		2.67			3.41
5	THF		2.88		3.60		2.50		2.75	3.07	
6		Na	2.77	$\Delta_{56} = -0.11$	3.72	$\Delta_{56} = 0.12$		2.60			3.32
7		Na c.c. ^c	2.65	$\Delta_{57} = -0.25$ $\Delta_{67} = -0.12$	3.89	$\Delta_{57} = 0.29$ $\Delta_{67} = 0.17$		2.75			3.50
8	DME		2.87		3.60		2.49		2.65	3.03	
9		Na	2.67	$\Delta_{89} = -0.20$	3.73	$\Delta_{89} = 0.13$		2.58			3.35
10		Li	2.79	$\Delta_{810} = -0.08$ $\Delta_{910} = +0.12$	3.76	$\Delta_{810} = 0.16$ $\Delta_{910} = 0.03$		2.61			3.30
11	Et ₂ O		2.93		3.59		2.48		2.70	3.07	
12		Mg	2.75	$\Delta_{1112} = -0.18$	3.63	$\Delta_{1112} = 0.04$		2.54			3.25

^a Chemical shifts are given in τ values (± 0.02 p.p.m.) relative to Me₄Si as internal standard for ca. 0.65M solutions. ^b Δ_{mn} Values refer to chemical shift differences between runs *m* and *n*. ^c 1,2:10,11-Bistetramethylene[18]crown-6 ether was used in equimolar amounts with the total alkali present.

two solvents, the above results can be accounted for on the basis that triazolyl and tetrazolyl anions can behave as proton acceptors, anions in methanol being thus more solvated than in dimethyl sulphoxide.

Indolyl Anions.—Great interest is currently attached to indole alkali-metal salts and to indole Grignard species. ¹H N.m.r. values for some of these species are reported in Table 3.

As expected 1,2:10,11-bistetramethylene[18]crown-6 ether displaces the equilibria (I) towards solvent-separated species; relative to indole, in these species the H(3) chemical shift has significantly moved upfield and is shown to be practically independent of the counterion and of solvent. Since the H(3) resonance in indole has been shown¹⁹ to be independent of association effects in different solvents, the H(3) resonance in indolyl anion can confidently be regarded as diagnostic in discriminating solvent-separated (C)/free indolyl ions (D) from contact (B)/covalent species (A). Both lithium and sodium salts of indole in tetrahydrofuran and dimethoxyethane show H(3) resonances as intermediate between the solvent-separated indolyl anions and neutral indole: thus, in these solvents and for these indolyl salts both

1,3-diphenylallyl anion:²¹ in this case a certain trend was observed from lithium to potassium on comparing results obtained at different temperatures: conclusions drawn can, however, be misleading as temperature has a profound effect on the equilibria (I).⁴ Moreover, extrapolation of conclusions obtained from spectra of carbanions to nitranions to infer the nature of the bond between the metal and the anionic centre is questionable since quite different results have been obtained¹¹ for fluorenyl anion and its aza-analogue, carbazolyl anion.

Indolylmagnesium iodide in ether is not appreciably different from the corresponding bromide in tetrahydrofuran: the resonance of H(3) does not suffer a significant shift relative to the precursor whilst those of H(5) and H(6) are only slightly shifted upfield, much less in fact than in alkali-metal salts. However, indolylmagnesium bromide was considered²⁰ more similar to the alkali-metal salts than to indole, despite the fact that it was noted²⁰ to be impossible to correlate consistently the proton chemical shifts within the

²⁰ M. G. Reinecke, J. Sebastian, H. W. Johnson, jun., and C. Pynn, *J. Org. Chem.*, 1971, **36**, 3091.

²¹ J. W. Burley, R. Iffe, and N. R. Young, *Chem. Comm.*, 1970, 1256.

¹⁹ M. G. Reinecke, H. W. Johnson, jun., and J. F. Sebastian, *J. Amer. Chem. Soc.*, 1969, **91**, 3817.

series. Intramolecular association was concluded²⁰ to be responsible for the behaviour of indolyl Grignard reagents. Since H(3) is practically invariant in indolyl Grignard species relative to indole, the only firm conclusion that can be inferred is that no solvent-separated ion-pairs contribute appreciably to the description of these species in the solvents considered. While upfield shifts of H(5) and H(6) can be better reconciled with intimate ion-pair (B) structures for Grignard indolyl species, results for H(3) and slow exchange (on n.m.r. time scale) experiments²⁰ with indole are compatible, as far as the ¹H n.m.r. technique is concerned, both with essentially covalent (A) and intimate ion-pair (B) representations. Whether indolyl Grignard species should be regarded as covalent or tightly bound ion aggregates still remains an intriguing point.

EXPERIMENTAL

Sodium and lithium salts in dimethyl sulphoxide were prepared according to the procedure previously described.²² In all cases alkali-metal methylsulphinyl carbanion was used in *ca.* 2 molar excess. Indolylmagnesium iodide was prepared by careful addition of a 2 molar excess of methylmagnesium iodide to indole. Sodium and lithium salts in other solvents were prepared by treating the substrate with an excess of sodium or lithium hydride in highly purified anhydrous (doubly distilled over lithium aluminium hydride) solvents. Spectra were recorded on Varian A60 A or HA 100 instruments.

Financial aid from C.N.R., Rome, is gratefully acknowledged.

[2/1463 Received, 23rd June, 1972]

²² S. Bradamante, A. Mangia, and G. Pagani, *J. Chem. Soc. (B)*, 1971, 545.