Pulsed Fourier-transformed ^{13}C Nuclear Magnetic Resonance Spectra of Methylsydnone and Related Compounds

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Natural abundance carbon-13 nuclear magnetic resonance spectra of several sydnones and related mesoionic compounds have been measured, the data indicating considerable shielding of C(4) in sydnones as predicted by earlier *ab initio* SCF–MO and semi-empirical MO calculations.

SIMPLE heterocyclic aromatic compounds have been of particular interest in ^{13}C chemical shift studies because of the electronic consequences of the heteroatom. Page, Alger, and Grant[1] were the first to discuss at length the ^{13}C data of furan, thiophen, and pyrrole, and their 2-methyl and 2,5-dimethyl derivatives. Subsequently reports have discussed the ^{13}C n.m.r. spectra of other five-membered heterocyclic compounds including further examples of furan,[2] thiophen,[3] and pyrrole[4] derivatives, as well as pyrazoles,[5] imidazoles,[6] and 1,2,3- and 1,2,4-triazoles,[2] and tetrazole.[2] Correlations of the observed chemical shifts with theoretically obtained parameters have been found[1,2,6,7] which suggest that ^{13}C chemical shifts are determined primarily by Hückel π-electron densities.

Five-membered mesoionic compounds have long attracted[8,9] interest because of their novel structure and their value as reactive intermediates in synthesis. As part of a study of these compounds we have examined the ^{13}C spectra of methylsydnone (1) and related compounds (2)—(7).

RESULTS AND DISCUSSION

In a recent re-formulation,[10] the sydnone system was postulated as a normal σ-framework extended through O(1)–N(2)–N(3)–C(4)–C(5), a weak C(5)–O(1) bond, and delocalization of 6 π-electrons over the ring atoms in preference to the mesoionic dipolar structures such as (8a), described earlier.[8,11–18] This re-formulation (8b)

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[1] T. F. Page, T. Alger, and D. M. Grant, *J. Amer. Chem. Soc.*, 1965, **87**, 5333.

[2] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1968, **90**, 3543.

[3] K. Takahashi, T. Sone, and K. Fujieda, *J. Phys. Chem.*, 1970, **74**, 2765; H. S. Jakobsen and O. Mancher, *Acta Chem. Scand.*, 1971, **25**, 680.

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[5] R. G. Rees and M. J. Green, *J. Chem. Soc. (B)*, 1968, 387.

[6] R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, 1968, **90**, 4332.

[7] B. M. Lynch, *Chem. Comm.*, 1968, 1337; J. E. Bloor and D. L. Green, *J. Amer. Chem. Soc.*, 1967, **89**, 6835; W. Adam, A. Grimison, and G. Rodriguez, *J. Chem. Phys.*, 1969, **50**, 645.

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[14] W. Baker, W. D. Ollis, U. D. Poole, J. A. Barltrop, R. A. W. Hill, and L. E. Sutton, *Nature*, 1947, **160**, 366.

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[16] R. Huisgen, R. Fleischmann, and A. Eikell, *Tetrahedron Letters*, 1960, 1.

[17] F. H. C. Stewart and N. Danieli, *Chem. and Ind.*, 1963, 1926.

[18] R. A. W. Hill, K. E. Sutton, and H. C. Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 244; L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113.

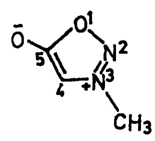
has been refined[19] to the formal representation (8c) on the basis of core-electron bonding-energies (ESCA) and *ab initio* SCF–MO and semi-empirical MO calculations on *N-methyl*sydnone. These calculations revealed a large degree of charge asymmetry in the molecule with considerable overlap populations between all bonded atoms. The theoretical parameters for C(4) all imply a high electron density at this carbon with the consequence of large diamagnetic shielding. The ^{13}C data determined in the present study provide evidence for this conclusion.

Carbon-13 chemical shifts * of some mesoionic systems

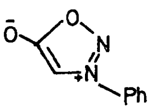
	Ring positions			Alkyl substituents		Aryl †			
Compound	2	4	5	6	7	1′	2′ + 6′	3′ + 5′	4′
(1)		96·77	169·2	39·75					
(2)		94·23	169·7			134·8	130·3	121·3	132·6
(3)		104·8	168·7	7·98		133·9	130·1	124·4	132·1
(4)		94·93	169·3	57·12		130·8	129·4	128·7	129·8
(5)		105·2	173·8	26·70	180·5	133·9	130·8	121·9	133·6
(6)	141·3	108·1	172·8	39·21		128·1	129·1	129·1	130·3
(7)	173·8		183·2	24·00	13·68	136·9	129·7	127·9	131·1

* In p.p.m. downfield from Me_4Si. † The carbon atoms in the phenyl groups in compounds (2)—(7) are numbered from 1′ (point of attachment) to 6′.

The extant data for the sydnones (1)—(5) and the related mesoionic ring systems (6)—(7) are presented in the Table. Assignment of the natural abundance resonances was made utilizing single-frequence off-resonance techniques, intensity measurements, and chemical shift data.[20]



(1)



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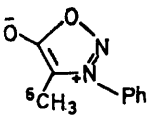

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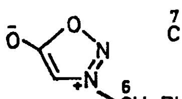

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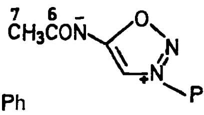

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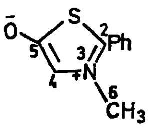

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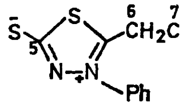

(7)

N-Methylsydnone has a simple three-line spectrum. The *N*-methyl carbon resonance occurs at +39·8 p.p.m., a value which reflects the strong deshielding effect of the nitrogen atom (*cf. N*-methylpyrazole at +38·3 p.p.m.).[5] The ring carbon atoms C(4) and C(5) resonated at +96·8 and +169·2 p.p.m. respectively. The chemical shift of C(4) is at considerably higher field than observed for the ring carbons of unsubstituted heterocycles[20] but completely consistent with the anticipated shielding effect. On the other hand, the chemical shift of the carbonyl carbon C(5), although at higher field than in normal ketones, occurs at a value similar to that observed[20] for the carbonyl carbons of lactones, amides, or imides. The substitution of simple five-membered heterocycles with electron donating substituents also results in a similar induced shielding of the β-carbon. For example, the C(2) and C(3) of 2-methoxythiophen,[3] in which mesomeric effects can operate, were observed at +167·9 and +104·8 p.p.m., respectively.

(8a) (8b) (8c)

Proposed structures * for 3-substituted sydnones (8)

* With the mesomeric betaine system, the contribution of several additional structures is implied.

An examination of the data of the other mesoionic compounds reveals further significant features of their aromatic structure. Replacement of the *N*-substituent in sydnones results in only a small variation of *ca.* 2·5 p.p.m. in the chemical shift of C(4) and very small shift differences for the exocyclic carbonyl carbon atom. Introduction of a C(4)-methyl group results in a downfield shift of the C(4) signal of *ca.* 10 p.p.m., *i.e.* the methyl group has a similar deshielding substituent effect on the attached C(4) carbon as has been noted with other benzenoid and heterocyclic aromatic compounds. The chemical shift of the C(4)-methyl itself reflects a considerable shielding effect of the C(4)-atom. When compared to a methyl substituent attached to furan (δ_C [CH_3] in 2-methylfuran 12·7 p.p.m.)[1] or other five-membered heterocycles, this represents a shift to higher field of *ca.* 5—8 p.p.m. Thus, the higher electron density predicted for C(4) becomes evident not only in the chemical shift of that atom but also in the chemical shift of the attached α-atom. The ^1H n.m.r. spectra of

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[19] M. Barker, J. J. Broadbent, J. A. Connor, M. F. Guest, I. H. Hillier, and H. J. Puxley, *J.C.S. Perkin II*, 1972, 1517.

[20] For compendia of carbon chemical shifts see G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972; J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

sydnones also are consistent with a shielding effect since the resonance [17,21] of the C(4) proton is at higher field than would be anticipated on the basis of the mesoionic structure (8a) or by analogy with other heterocycles. With *N*-[3-phenyl-5-(1,2,3-oxadiazolio)]acetamidate (5) a shift of the C(4) and C(5) signals to lower field would be anticipated owing to the decreased inductive effect and extended delocalization of the $CH_3CO{\cdot}N$ group, and was observed with downfield shifts of 11·0 and 4·1 p.p.m., respectively, compared to the corresponding carbons of the 5-oxa-analogue. The thia-analogues (6) and (7) exhibit spectral features similar to the sydnones; the presence of the ring sulphur atom results in a general shift of the ring carbon signals to lower field, indicative of greater polarization of charge and regionalized dipolar character in the molecule, and this is mirrored in their chemical properties.[9]

Several conclusions can be drawn from the present results. First, the chemical shift data are consistent with the most recent refinements [19] in the structure of sydones. Although the formal representation (8a) will probably persist as the most commonly used and convenient structure, due caution must be used in its application since it implies a positive charge associated with the ring and a net deshielding effect on each of the ring atoms. Secondly, the range $\delta_C^{Me_4Si}$ 94·2—96·8 for the unsubstituted C(4) in the compounds examined is indicative of the high electron density at this carbon. The chemical shifts of the ring carbons provide further support for the suggestion that ^{13}C shifts of aromatic compounds are determined predominantly by the π-contribution to the electron density. Thirdly, variation in the quaternary nitrogen substituent (Me, Ph, $PhCH_2$) appears to cause smaller differences in the chemical shift of the ring carbons of mesoionic compounds than observed for neutral tertiary nitrogen heterocycles, *e.g.* 1-substituted pyrazoles.

EXPERIMENTAL

^{13}C Fourier spectra were recorded on a Bruker HFX multinuclear spectrometer operating at 22·63 MHz. The spectra were obtained by storing the free induction decays produced by a series of 10 μs r.f. pulses in a Fabritek 1074 computer of average transients. The interferograms which result were then Fourier transformed by a Digital PDP 81 computer.

The compounds were measured as 20—25% (w/w) solutions in deuteriochloroform containing *ca.* 5% Me_4Si (w/w). The data recorded are in p.p.m. downfield from the carbon resonances of the internal tetramethylsilane and are thought to be accurate to ±0·2 p.p.m. Compounds (1)—(7) were prepared [8,22] by reported procedures and were purified immediately prior to use.

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