Deshielding of Carbon-13 Nuclei by Attached Iodine Atoms. Solvent Effects on Carbon-13 Chemical Shifts in Alkyl Iodides

By ANTHONY MARKER, DAVID DODDRELL,* and N. V. RIGGS

(*Department of Organic Chemistry, University of New England, Armidale, N.S.W.*, 2351, *Australia*)

Summary Deshielding of carbon-13 nuclei occurs upon replacement of hydrogen by iodine at secondary and tertiary carbon atoms and may be related to the low electron density at the carbon atom as a consequence of the highly ionic character of the C–I bond in these cases; large solvent effects occur at the carbon atom directly bonded to iodine and affect substituent-effect parameters, the solvent shift varies linearly with the Onsager reaction-field.

PREVIOUS studies on alkyl[1–5] and aryl[6,7] iodides by ^{13}C n.m.r. spectroscopy have all emphasized that replacement of hydrogen by iodine results in shielding at the directly bonded carbon atom. The substituent-effect parameter, A^{I}_{α}, defined by $A^{\mathrm{I}}_{\alpha} = \delta^{\mathrm{I}}_{\alpha} - \delta^{\mathrm{H}}_{\alpha}$, where $\delta^{\mathrm{I}}_{\alpha}$ and $\delta^{\mathrm{H}}_{\alpha}$ are chemical shifts relative to the same reference for the α-carbon atom in the iodo-compound and the corresponding hydrocarbon, respectively, ranges from *ca* +6 p.p.m. for primary alkyl iodides[3] to *ca* +42 p.p.m. for acetyl iodide.[5] Solvent effects on ^{13}C chemical shifts have been reported for various systems[2,8–12]; solvent shifts observed were small (less than, say, 1 p.p.m.) except where hydrogen bonding occurred[9,10] or for the cases of CH_3Br[2] and CH_3I[2,8].

We have now measured proton noise-decoupled, natural-abundance ^{13}C n.m.r. spectra of some representative alkyl iodides in various solvents (see Table). The solvent shift Δ_i refers to the upfield shift of the signal for the *i*th nucleus for a dilute solution in the given solvent (or for the neat liquid) relative to the same signal for a dilute solution in cyclohexane. For each iodide studied solvent shifts for the α-(iodine-bearing) carbon atom are large (2·5 p.p.m. or more) and negative, *i.e.* the signals appear at lower fields for solvents more polar than cyclohexane. Buckingham[13] has predicted, on the basis of the Onsager model[14] for the reaction field of a polar molecule in a medium of dielectric constant ϵ, that ^{13}C screening constants in substituted methanes should depend linearly on the function, $(\epsilon - 1)/(2\epsilon + n^2)$, where n is the refractive index of the solute molecule. The prediction[13] appeared to fail to account for solvent dependence of ^{13}C chemical shifts for CH_3I and

CH_3CN,[8] but the choice of solvents in that work has been criticized.[15] For the limited number of solvents so far used in the present work, solvent shifts for the α-carbon atoms are in fact reasonably linear functions of $(\epsilon - 1)/(2\epsilon + n^2)$, where ϵ is the dielectric constant as calculated[16] from the known composition of the solution and the dielectric constants of its components. Smaller but still appreciable downfield solvent shifts (up to 0·9 p.p.m.) or, in one case, a small upfield shift (0·1 p.p.m.) are observed for the terminal methyl (ω-) carbon atoms, but we cannot rationalize these effects simply. Solvent shifts for the remaining carbon atoms are small (0·1 — 0·2 p.p.m.).

TABLE. *Carbon-13 shifts*[a] *and some derived parameters for alkyl iodines.*

Alkyl iodide	Solvent[b]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Δ_α^c	Δ_ω^c	$A_\alpha^{\mathrm{I}c}$
1-Iodoethane	C	198·1	172·9								+10·9
	N	193·9	172·0						−4·2	−0·9	
	NM	193·7	172·7						−4·4	−0·2	
	DMF	192·9	172·2						−5·2	−0·7	
1-Iodopentane	C	189·4	159·4	160·1	171·3	179·7					+10·1
	N	186·6	159·3	160·0	171·1	178·9			−2·8	−0·8	
	NM	185·5	159·2	160·0	171·2	179·6			−3·9	−0·1	
	DMF	185·0	159·2	160·0	171·2	179·2			−4·4	−0·5	
1-Iodoheptane	C	189·2	159·0	162·2	164·5	161·0	170·3	179·4			+10·1
	N	186·7	159·0	162·2	164·5	161·0	170·2	178·8	−2·5	−0·6	
	NM	185·4	158·9	162·2	164·5	161·0	170·2	179·3	−3·8	−0·1	
	DMF	184·8	158·8	d	164·5	160·9	170·2	179·0	−4·4	−0·4	
2-Iodopropane	C	161·9[e]	175·6								− 1·4
	N	161·1[e]	172·3						−3·3	−0·8	
	NM	162·0[e]	170·1						−5·5	+0·1	
	DMF	161·6[e]	169·7						−5·9	−0·3	
2-Iodo-2-methylpropane	C	152·6[f]	154·2								−13·7
	N	151·7[f]	150·8						−3·4	−0·9	
	NM	152·6[f]	147·1						−7·1	0·0	

[a] In p.p.m. upfield from CS_2. Values are for dilute (*ca.* 0·05 mole fraction) solutions or the neat liquids; [b] C = cyclohexane; N = neat liquid; NM = nitromethane; DMF = *NN*-dimethylformamide. The last three contained a trace of cyclohexane as internal reference; [c] As defined in the text; [d] Obscured by DMF resonance; [e] Two-carbon resonance; [f] Three-carbon resonance.

As large solvent effects on ^{13}C chemical shifts may occur, in general substituent-effect parameters calculated without regard to the solvents used should be treated circumspectly. Values of A_α^{I} given in the Table have been calculated from chemical shifts for dilute solutions of the iodides in cyclohexane and literature values[2,17,18] for the parent alkanes for which we assume solvent shifts may be neglected. Whereas replacement by iodine of hydrogen in a methyl group results in shielding of the carbon atom by 10—11 p.p.m., similar substitution at a secondary or tertiary carbon atom may produce a large deshielding effect. The change from shielding for 1-iodoethane to deshielding for 2-iodopropane and 2-iodo-2-methylpropane may be stated in the alternative form that successive methyl substituents at the α-carbon atom each produce a change of −12·3 p.p.m. in A_α^{I}. Mason[19] has proposed that shielding of ^{13}C nuclei on attachment to iodine arises because local electron circulations on the iodine atom make additional contributions to the diamagnetic component of the ^{13}C screening tensor. Presumably, then, deshielding in the above cases is due to even greater contributions to the paramagnetic component of the screening tensor such as would result from a decrease in electron density at the carbon atom owing to an increase in ionic character of the C–I bond.[20,21] Evidence for the latter increase is found in the substantial decreases in iodine quadrupole coupling constants upon successive methyl substitution at the α-carbon atom in alkyl iodides.[22]

This work is being extended to a variety of solute-solvent systems. We thank Professor R. H. Stokes for useful discussions, and the Australian Research Grants Committee for financial support.

(*Received*, 10*th April* 1972; *Com.* 595.)

[1] P. C. Lauterbur, *Ann. New York Acad. Sci.*, 1958, **70**, 841.
[2] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 722.
[3] T. D. Brown, Ph.D. Thesis, University of Utah, 1966.
[4] W. M. Litchman and D. M. Grant, *J. Amer. Chem. Soc.*, 1968, **90**, 1400.
[5] G. E. Maciel, *J. Chem. Phys.*, 1965, **42**, 2746.
[6] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.
[7] P. C. Lauterbur, *J. Chem. Phys.*, 1963, **38**, 1406.
[8] J. K. Becconsall and P. Hampson, *Mol. Phys.*, 1965, **10**, 21.
[9] G. E. Maciel and D. D. Traficante, *J. Amer. Chem. Soc.*, 1966, **88**, 220 and references therein.
[10] R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, 1970, **74**, 912.
[11] M. Bacon, G. E. Maciel, W. K. Musker, and R. Scholt, *J. Amer. Chem. Soc.*, 1971, **93**, 2537.
[12] G. C. Levy and J. D. Cargioli, *J. Magnetic Res.*, 1972, **6**, 143.
[13] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.
[14] L. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.
[15] P. Laszlo, *Progr in N.M.R. Spectroscopy*, 1967, **3**, 231.
[16] D. Decroocq, *Bull. Soc. chim. France*, 1964, 127.
[17] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.
[18] L. P. Lindeman and J. Q. Adams, *Analyt. Chem.*, 1971, **43**, 1245.
[19] J. Mason, *J. Chem. Soc. (A)*, 1971, 1038.
[20] J. A. Pople, *Mol. Phys.*, 1963, **7**, 301.
[21] B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 5319.
[22] W. Zeil, W. Hüttner, and W. Plein, *Z. Naturforsch.*, 1962, **17a**, 823.