Tetrahedron Letters No.53, pp. 5541-5544, 1968. Pergamon Press. Printed in Great Britain.

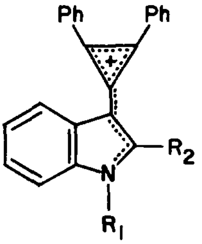
AZAPENTATRIAFULVALENIUM IONS. II. STRUCTURE AND STABILITY

Merle A. Battiste (1) and John H. M. Hill (2)

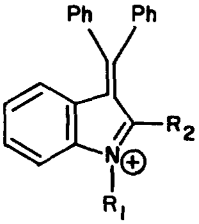
Department of Chemistry, University of Florida, Gainesville, Florida 32601

(Received in USA 3 September 1968; received in UK for publication 26 September 1968)

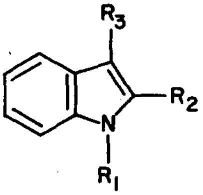
In the preceding communication we described a convenient synthesis of azapentatriafulvalenium salts, I. (3) Herein we consider the charge distribution in I. Formulation of compounds similar to I as indolium salts has been proposed by several workers (4,5) while Kende, et al., consider these to be more precisely described as 3-indolylcyclopropenium salts. (6) Our evidence, based on (a) comparison of the nmr spectra of I, 3-benzhydrylidene-3H-indolium salts (II), (7) and their common indole precursors (III) (Table 1), and (b) pK_{R^+} values determined for I and for various cyclopropenium salts (8) (Table 2), suggests that the best description of these compounds involves extensive delocalization of charge throughout the cyclopropene and heterocyclic rings, as shown in I.



I

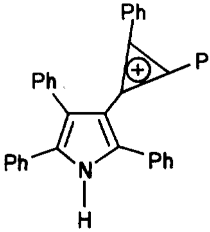


II

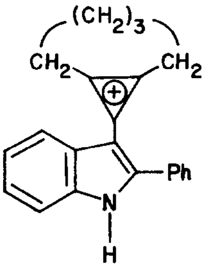


III

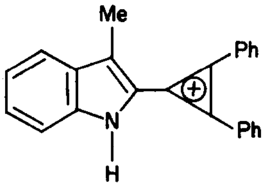
Consistent with our formulation, groups substituted on the heterocyclic ring show pronounced downfield shifts in the nmr due to deshielding by the partially charged ring. (9) For example, while the N-H protons of III are in the range $\tau 1.7 - 2.6$, those for Ia, Ib, and Id range from τ -5.3 to -3.6. Similarly, the $N\text{-}CH_3$ signals of Ic and Ie are about 1 ppm downfield from those of IIIc and IIIe, as are those of IIb and IIc, which must have the charge largely localized on the heterocyclic nitrogen. Interestingly, methyl groups at the 2-position of Ib and Ic are



IV



V



VI

Table 1

NMR Data (τ-Values)

Compounds, with Substitution		R	R_2 or Ph	R_3 or Ph
Ia	$R_1=R_2=H$	-4.96[a]	0.29	1.62, 2.04, 2.46
Ib	$R_1=H$, $R_2=Me$	-4.94[a]	6.91	1.64, 2.02, 2.46
Ic	$R_1=R_2=Me$	5.92	6.91	1.64, 2.00, 2.35
Id	$R_1=H$, $R_2=Ph$	-5.31[a]	2.37	2.16
Ie	$R_1=Me$, $R_2=Ph$	5.98	2.25	2.25
IIa	$R_1=H$, $R_2=Me$	----	7.68	2.49, 2.96
IIb	$R_1=R_2=Me$	5.92	7.70	2.39, 2.95
IIc	$R_1=Me$, $R_2=Ph$	6.00	2.70	2.37, 2.80
IIIa	$R_1=R_2=R_3=H$[a]	2.40	3.31	3.55
IIIb	$R_1=R_3=H$, $R_2=Me$[a]	2.50	7.81	3.85
IIIc	$R_1=R_2=Me$, $R_3=H$[a]	6.70	7.80	3.84
IIId	$R_1=R_3=H$, $R_2=Ph$[a]	1.80	2.6	3.23
IIIe	$R_1=Me$, $R_2=Ph$, $R_3=H$[a]	6.47	2.63	3.49
IIIf	$R_1=R_2=H$, $R_3=Me$[a]	2.6	3.22	7.72
IV		-3.55[c]	----	2.61
VI	$R_1=H$, $R_3=Me$	-1.35	1.48, 1.99, 2.25[b]	6.94
2,3,5-Triphenylpyrrole		1.77[c]	2.73[b]	3.34[d]
Triphenylcyclopropenium bromide		----	----	1.36, 1.89
Diphenylcyclopropenone		----	----	2.04, 2.41[a]
Diphenylcyclopropenone		----	----	1.83, 2.22
Diphenylcyclopropenone		----	----	1.64, 2.10[e]

[a] in $CDCl_3$, otherwise in TFA (spectra in TFA and $CDCl_3$ were essentially the same for compounds soluble in both), [b] Ph signal, [c] N-H signal, [d] C-H signal, [e] in FSO_3H.

Table 2

$\mathrm{p}K_{R}+$ and UV Data in 50% Aqueous Ethanol

Compound	(Ph)$_3$	VI	Id	Ic	Ib	Ia	IV	V	(p-Anis.)$_3$
$\mathrm{p}K_{R}+$	1.62	2.24	4.71	4.87	4.91	5.21	5.45	6.52	5.24
λ_{max}^{cation}, nm	308	374	367	357	354	353	373, 288	337	359
log ε	4.67	4.59	4.34	4.50	4.46	4.55	4.02, 4.58	4.27	4.86

shifted downfield about 1 ppm, whereas those of IIa and IIb are not. This suggests either that there is little positive charge at the 2-position of II or that the phenyl rings of the benzhydrylidene group in II exert a compensating shielding effect on the 2-methyl substituent. That the latter is the important effect is supported by models which show that while the phenyl groups of II must be severely twisted from the plane of the indole ring those of I are sufficiently remote from the 2-methyl substituent that they can become coplanar with the indole ring.

Evidence that significant positive charge resides in the cyclopropene ring is provided by the chemical shift pattern of the aromatic region for derivatives of I not substituted in the 2-position by a phenyl group. The diphenylcyclopropene protons are observed at lower overall field than comparable examples of II or diphenylcyclopropenone and are split into characteristic low field (ortho) and high field (meta-para) components, while the benzo protons appear at still higher field in the usual aromatic region. An almost identical low field aromatic pattern is exhibited by the triphenylcyclopropenium cation and by protonated diphenylcyclopropenone. The downfield shifts of Ia-c and the chemical shift differences between their ortho and meta-para components are intermediate between those of the neutral and cationic cyclopropenium models given in Table 1.

The above data suggest extensive charge distribution for azapentatriafulvalenium ions. The nmr spectrum of V further supports this view. Below 40° the methylene groups adjacent to the cyclopropene ring are nonequivalent due to restricted rotation. The 2-phenyl substituent shields the closest methylene, which appears as a broad singlet at τ 7.15, whereas the other terminal methylene is at 6.67 with the remainder of the methylene bridge appearing at 7.91. This spacing of about 1.3 ppm is consistent with appreciable cyclopropenium ion character.(10) The flanking phenyl groups on the heterocyclic ring of Id, Ie, and particularly IV exert a similar effect on the protons of the phenyls attached to the cyclopropene ring, which are shielded and appear at relatively higher fields. Also, the characteristic pattern of ortho and meta-para protons which is observed if the 2-substituent is hydrogen or methyl is lost.

Ions I, IV, and V react reversibly in aqueous buffer solutions to yield the corresponding triarylcyclopropenols, as evidenced by the well defined isosbestic points in the uv spectra of these solutions. The pK_{R^+} values derived from these spectra are compatible with extensive delocalization of charge into the heterocyclic ring, the substitution of an indole or pyrrole ring for a phenyl resulting in an apparent increase in stability corresponding to 3 to 5 pK units. This effect is comparable to replacement of all phenyl rings by p-anisyl groups.(11) In VI, where delocalization of the charge onto nitrogen would involve an o-quinonoid indolium ion, little gain in stability is found, which parallels the nmr data for this ion. Thus the downfield shift of the N-H proton in VI is not as great as in I, and the protons of the phenyl groups attached to the cyclopropene ring occur at lower field than in I and are comparable to arylcyclopropenium cations.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. Alfred P. Sloan Foundation Fellow, 1967 - 1969.
2. On leave from Hobart and William Smith Colleges, Geneva, N. Y., 1967 - 1968.
3. J. H. M. Hill and M. A. Battiste, "Azapentatriafulvalenium Ions. Part I." accompanying communication, 5537 (1968).
4. T. Eicher and A. Hansen, Tetrahedron Letters, 4321 (1967).
5. R. Gompper and R. Weiss, Angew. Chem., **80**, 277 (1968).
6. A. S. Kende, P. T. Izzo and P. T. MacGregor, J. Am. Chem. Soc., **88**, 3359 (1966).
7. M. Freund and G. Labach, Ber., **38**, 2646 (1905); G. O. Burr and R. A. Gortner, J. Am. Chem. Soc., **46**, 1224 (1924).
8. Determined spectrophotometrically in 50% aqueous ethanol due to the insolubility of the carbinols in water (A. Albert and E. P. Serjeant, Ionization Constants of Acids and Bases, p. 69, Wiley, New York (1962)). Notwithstanding the pitfalls of pK determinations in mixed solvents and the lack of information regarding the free energies of the carbinols, we feel that the comparisons of pK and cation stability are meaningful and internally consistent.
9. G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richard, J. Am. Chem. Soc., **82**, 5846 (1960).
10. R. Breslow, H. Hover and H. W. Chang, ibid., **84**, 3168 (1962).
11. R. Breslow, J. Lockhart and H. W. Chang, ibid., **83**, 2375 (1961).