Tetrahedron Letters, Vol.27, No.1, pp 11-14, 1986
Printed in Great Britain

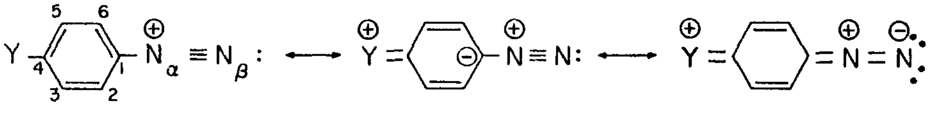
0040-4039/86 $3.00 + .00
©1986 Pergamon Press Ltd.

# SUBSTITUENT EFFECTS ON $^{13}C$-$^{15}N$ SPIN COUPLINGS AND $^{13}C$ CHEMICAL SHIFTS IN BENZENEDIAZONIUM IONS

T. Axenrod, X. H. Huang and C. Watnick
Department of Chemistry
The City College of the City University of New York
New York, N.Y. 10031

Abstract: Similar trends are observed for $^1J(^{13}C$-$^{15}N)$ values for a series of aryldiazonium tetrafluoroborates and comparable anilinium fluorosulfonates. Contributions from resonance structures involving double-bond character in the C-N bond are judged to be relatively unimportant in the ground state structure of aryldiazonium ions.

The structure and bonding in benzenediazonium ions have been extensively investigated by a variety of spectroscopic methods[1] including $^1H$, $^{13}C$ and $^{15}N$ NMR.[2-5] The latter two techniques have proven to be particularly sensitive probes of the electronic environments of the carbon and nitrogen nuclei, although the reports that have appeared in the literature to date have been essentially confined to the influence of aromatic ring substituents, solvents, anions and complexing agents on the respective chemical shifts of these nuclei. The instability and low solubility of uncomplexed benzenediazonium salts in most organic solvents, combined with the need for $^{15}N$-enriched compounds, may have deterred the study of the $^{15}N$-$^{13}C$ spin-spin couplings in these systems despite the potentially new information that could be obtained.



Ia Ib Ic

We report here the preliminary results that have recently been obtained in these laboratories for a series of double $^{15}N$-labelled (>95% enrichment) benzenediazonium tetrafluoroborates in N,N-dimethylformamide/deuteriobenzene solution. The aryldiazonium fluoroborates were synthesized by standard procedures[9] from the respective $^{15}N$-labelled anilines[10] and

Table I. $^{13}$C Chemical Shifts and $^{13}$C-$^{15}$N Coupling Constants of Benzenediazonium Tetrafluoroborates[a] and Anilinium Fluorosulfonates[b]

| Substituent | $^{13}$C-$^{15}$N Coupling Constants[c] | | | | | Chemical Shift[d,e] |
|---|---|---|---|---|---|---|
| | Anilinium ion | Benzenediazonium ion | | | | |
| Y | $^1J(C_1N)$ | $^1J(C_1N_\alpha)$ | $^2J(C_1N_\beta)$ | $^2J(C_2N_\alpha)$ | $^3J(C_3N_\alpha)$ | $C_1$ |
| 2,4,6-$(Br)_3$ | 13.5 | 19.8 | 6.1 | 2.0 | --[f] | 120.6 |
| 4-$(CH_3)_2N$ | --- | 17.9 | 5.1 | 2.0 | 2.6 | 89.4 |
| 2-Cl, 4-$NO_2$ | --- | 15.6 | 5.9 | ---[f] | 3.3(2.0)[g] | 122.7 |
| 2-Br | 11.0 | 14.5 | 6.1 | ---[f] | ---[f] | 118.8 |
| 4-$CH_3O$ | --- | 14.4 | 5.8 | 2.0 | 2.9 | 103.7 |
| 3-$NO_2$ | --- | 12.9 | 5.6 | 3.0 | 3.7(3.3)[g] | 118.6 |
| 4-Br | 9.2 | 12.1 | 5.6 | 2.3 | 3.1 | 115.4 |
| 4-$NO_2$ | 9.2 | 11.4 | 5.6 | 2.7 | 3.2 | 122.3 |
| 3,5-$(CH_3)_2$, 4-$NO_2$ | --- | 11.4 | 5.8 | ---[f] | 3.3 | 118.7 |
| 3-Br | 7.9 | 11.2 | 5.5 | 3.3 | 4.0(1.9)[g] | 118.1 |
| H | 8.6 | 10.5 | 5.6 | 2.1 | 3.0 | 116.4 |
| 3,5-$(CH_3)_2$ | --- | 10.0 | 5.8 | 2.1 | 3.2 | 115.3 |

[a] Measurements made at 5°C using 0.20 M solutions in 93:7 (weight %) N,N-dimethylformamide: deuteriobenzene. [b] In $HFSO_3$ solution, data taken from reference 8. [c] In Hz, ±0.3 Hz. [d] Chemical shifts are for the benzenediazonium ion. [e] In ppm, measured from deuteriobenzene and reported against TMS. [f] Not resolved due to overlap of signals. [g] $^2J(C_6N_\alpha)$.

Na$^{15}$NO$_2$. The $^{13}$C-$^{15}$N coupling constants and $^{13}$C chemical shifts measured at 50(?) MHz using an IBM WP-200SY spectrometer are summarized in Table I. In agreement with earlier findings,[6] electron-releasing substituents cause an upfield shift in the C-1 resonance and this has been interpreted in terms of an increased contribution of resonance structures such as Ic to the hybrid ground state structure. However, neither X-ray studies nor IR spectroscopy provide much support for major contributions from diazo-type structures (Ic) because the $C_1N_\alpha$ bond is found to be an ordinary single bond and the $N_\alpha$-$N_\beta$ bond length and stretching frequencies are those of a normal triple bond.[7] Thus, the accumulated evidence favors the ground state structure of the diazonium ion weighted in terms of resonance forms Ia-Ib.

It is significant that the data collected in Table I show that only the one-bond coupling is sensitive to the ring-substituent, with values of $^1J(^{13}C-^{15}N)$ ranging from 10.0 Hz in the 3,5-dimethylbenzenediazonium ion to 19.8 Hz in the 2,4,6-tribromo derivative and that the magnitude is enhanced by both electron-withdrawing and releasing substituents Moreover, to the extent that data are available for comparable substitutents, a striking parallel is found in the $^1J(^{13}C-^{15}N)$ values measured in these diazonium ions and those that were previously reported for anilinium ions.[8] For comparison, data for the anilinium ions are also included in Table I.

Lone pair effects in aromatic azo and diazo compounds are known to have a marked influence on $^1J(^{13}C-^{15}N)$.[11] Therefore, from the similarity of substituent effects in diazonium ions, anilinium ions, but not in anilines, and the fact that structures involving formal C=N double bonds are not possible in protonated anilines, it may be concluded that similar coupling mechanisms are operating and that this strengthens the case against the importance of diazo type structures such as Ic.

It is also interesting to note that when the resonance interaction of the nitro group is sterically inhibited, as is the case in the 3,5-dimethyl-4-nitrobenzenediazonium ion, the C-1 carbon experiences considerably reduced deshielding, but the magnitude of $^1J(^{13}C-^{15}N)$ is unaffected. Again, this suggests that there is no significant change in the $C_1$-N bond order, at least with electron-attracting substituents.

Preliminary INDO-MO calculations[12] indicate that $^1J(^{13}C-^{15}N)$ has the expected negative sign and that the coupling mechanism is dominated by the Fermi contact term. These results will be reported at a later date along with the effect of complexing agents.

Acknowledgment

This work was supported by a PSC-CUNY grant.

References:

1. D. A. Ben-Efraim in "The Chemistry of Diazonium and Diazo Groups;" S. Patai, Ed., Wiley, New York, 1978; Part I, Chapter 5.
2. G. A. Olah and J. L. Grant, J. Amer. Chem. Soc., 97, 1546 (1975).
3. A. M. Elofson, N. Cyr, J. K. Laidler, K. F. Schulz and F. F. Gadallah, Can. J. Chem., 62, 92 (1984).
4. C. Casewit, J. D. Roberts, and R. A. Bartsch, J. Org. Chem., 47, 2875 (1982).
5. S. H. Korzeniowski, A. Leopold, J. R. Beadle, M. F. Ahern, W. A. Sheppard, R. Khanna and G. W. Gokel, J. Org. Chem., 46, 2153 (1981).

6. R. O. Duthaler, H. G. Forster and J. D. Roberts, J. Amer. Chem. Soc., 100, 4974 (1978).

7. S. Sorriso in "The Chemistry of Diazonium and Diazo Groups," S. Patai, Ed., Wiley, New York, 1978; Part I, Chapter 3.

8. T. Axenrod, M. J. Wieder, T. Khin, G. A. Webb, H. J. C. Yeh and S. Bulusu, Org. Magn. Reson., 12, 1 (1979).

9. A. Roe, Org. React., 5, 193 (1949).

10. T. Axenrod, P. S. Pregosin, M. J. Wieder, R. B. Bradley, E. D. Becker, and G. W. A. Milne, J. Amer. Chem. Soc., 93, 6536 (1971).

11. S. Simova, E. Fanghanel and R. Radeglia, Org. Magn. Reson., 21, 163 (1983).

12. G. A. Webb, personal communication.

(Received in USA 20 August 1985)