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# PROTON MAGNETIC RESONANCE SPECTRA OF SOME BISAMINATED BENZOQUINONES

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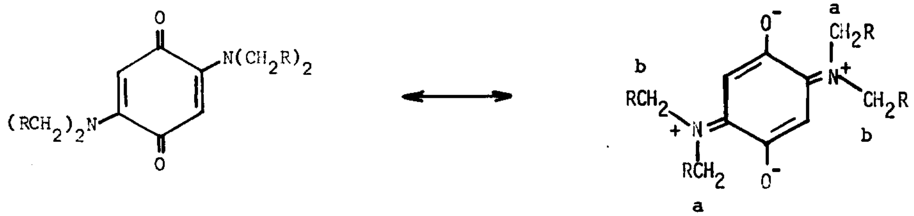
Evidence[1,2,3,4] has been adduced in support of significant quandrupolar resonance contributors (1) to the structures of 2,5-bisaminated-1,4-benzoquinones (2). We have measured $^1H$ n.m.r. spectra of a series of such compounds (3) - (7) which affords a means of comparing the effects on the quinone nucleus of an homologous series of cyclic secondary amino substituents. It has already been argued that for these compounds shielding of the quinonoid protons is an effective measure of the importance of contributors such as (1) and our results, given in the Table, are substantially in agreement with those reported by Dähne _et al_.[2] It is noteworthy that, of the compounds studied, shielding is greatest in the azetidino case (4), data for which are reported for the first time.



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Interesting results may also be obtained from variable temperature measurements. At the upper end of the temperature range all protons of the $CH_2N$ ($CH_3N$) groupings were observed as singlets. In all but the aziridino compound (3) lowering of the sample temperature to -60°C caused these signals to broaden and in some cases to separate into two distinct multiplets of equal intensity and centred ~60 Hz apart. Approximate coalescence temperatures (Tc) are shown in the Table. This change is attributed to contributions such as (1) enabling differentiation between groupings _a_ and _b_ and the relative Tc values suggest that the significance of such contributions decreases in the order azetidino > pyrrolidino > dimethylamino > piperidino > aziridino. The relative position of the three-, five-, and six-membered ring substituents is in agreement with reported observations.[2] Analogous systems substituted by azetidine are less well investigated, however, and the position of this grouping at the head of the series by both the criteria discussed here warrants closer examination. The effectiveness of electron donation by azetidino nitrogen might usefully be employed elsewhere, for example in enamine chemistry.

TABLE

| $N(CH_2R)_2$ | Tc(°C) | quinone H (τ) |
|---|---|---|
| aziridino (3) | $<-60$ | 4.05 |
| azetidino (4) | 65 | 5.08 |
| pyrrolidino (5) | 25 | 4.75 |
| piperidino (6) | $<-60^*$ | 4.50 |
| dimethylamino (7) | -45 | 4.67 |

*broadening but no discernible separation at -60°. All spectra measured at 100 MHz in $CDCl_3$.

Quinones having greater contributions from (1) would be expected to have lower oxidation potentials. Experimental evidence supporting this within the series is obtained when amine and quinone are reacted together in the presence of air, the bisaminated quinones being the sole amination products isolated in compounds (4), (5) and (7), while with aziridine and piperidine, substantial quantities of the corresponding quinols are also obtained.[5] The accompanying communication involves polarographic studies on compounds (3) - (7) and *inter alia* the results indicate that resistance to reduction (or corresponding ease of oxidation) decreases in approximately the same order encountered above.

## REFERENCES

1. D. Leupold and S. Dähne, *Theor. Chem. Acta*, 3, *1* (1965).
2. S. Dähne, J. Ranft, and H. Paul, *Tetrahedron Letters*, 3355 (1964).
3. S. Kulpa, D. Leupold, and S. Dähne, *Angew. Chem. Int. Ed.*, *5*, 599 (1966).
4. S. Dähne and D. Leupold, *Angew Chem. Int. Ed.*, *5*, 984 (1966).
5. A. Marxer, *Helv. Chim. Acta*, *38*, 1473 (1955).