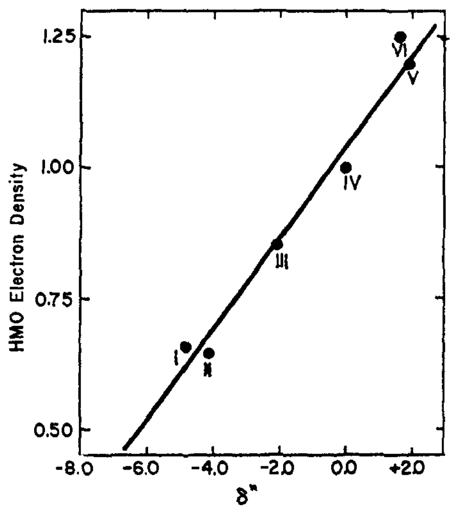

Figure 1. Plot of HMO π electron density *vs.* δ'' for I, di-*n*-cyclopropenium perchlorate; II, 2,6-dimethylhepatrienyl cation; III, tropylium fluoroborate; IV, benzene; V, sodium cyclopentadienide; and VI, dipotassium cyclooctatetraenide.

value of δ'' for the π complex (HMO π electron density 0.500) of -6.25 ppm with a probable error of 0.23 ppm. While we have not corrected the reported chemical shifts for the variation in solvent, nor for the effects of the counterion, the satisfactory linear fit of the data in Figure 1 indicates that such variations are probably not of substantial importance as compared with the molecular effects. In addition the expected changes in hybridization due to the angular distortion in the cyclopropenium and cyclooctatetraenide systems and the satisfactory fit of these data to Figure 1 appear to indicate that such effects are also minor, in part justifying our earlier assumption.

The comparison of the predicted downfield shift of approximately 6.6 ppm for the π complex and the observed shift of approximately 1.0 ppm leads to the conclusion that the π complex may contribute as much as 15% to the total electronic structure of **1**. In the absence of further information, we are of the opinion that this is the electronic structure most consistent with the facts. The apparent substantial contribution of the π complex to the electronic structure of **1** gives us confidence that this effect will be thermodynamically observable in the equilibrium studies currently in progress and that this may be but one of a series of compounds which exhibit aromatic character *via* cyclopropyl conjugation.

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R. A. Clark, R. A. Fiato[19]
Department of Chemistry, Clarkson College of Technology
Potsdam, New York 13676

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Interpretation of Biradical Electron Resonance Spectra

Sir:

Ferruti, *et al.*, have measured the electron resonance spectra of the nitroxide biradicals I–III as a function of pH.[1] The spectra exhibit a slight pH dependence because the polar groups may be ionized or neutralized, thus changing the nature of the chain linking the nitroxides. Their interpretation of the spectral changes is, at best, incomplete or, at worst, incorrect.

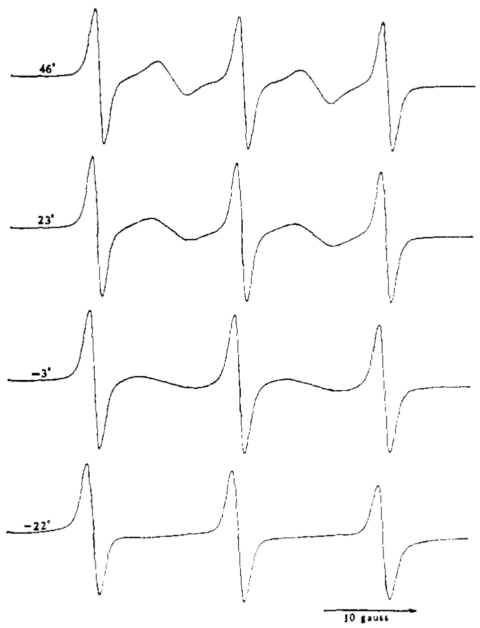
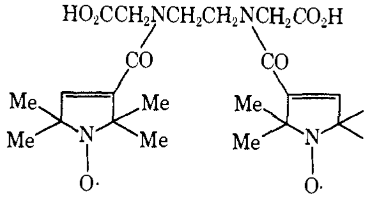
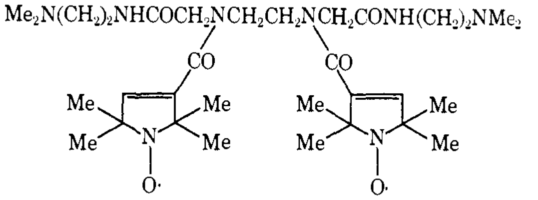


Figure 1. The electron resonance spectrum of bis(2,2,6,6-tetramethylpiperidin-4-ol) glutarate as a function of temperature.



I



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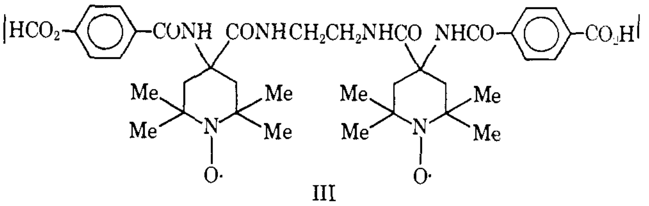
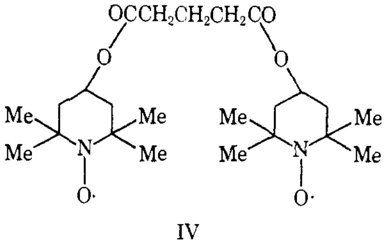


III



IV

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[1] P. Ferruti, D. Gill, M. P. Klein, and M. Calvin, *J. Amer. Chem. Soc.*, **91**, 7765 (1969).

The electron resonance spectra of I and II in their ionized forms are similar to that of bis(2,2,6,6-tetramethylpiperidin-4-ol) glutarate (IV) at 23° (Figure 1). In the un-ionized forms the widths of the second and fourth lines have decreased and the spectra resemble that of IV at 46°. The observation of five equally spaced spectral lines shows that the spin exchange, $\bar{J}$, is much greater than the nitrogen coupling constant, a, and so $\bar{J}$ cannot be determined from the spectrum. However, the heights and hence widths of the lines are said to be a measure of the spin exchange. It is clearly impossible to make such an interpretation without examining the factors which determine the line widths.

Except at low temperatures the dominant relaxation mechanism for flexible biradicals is modulation of J *via* the intramolecular motion.[2] When $\bar{J} \gg a$ the electron resonance spectra exhibit line-width alternation as shown in Figure 1. The width of the second and fourth lines is given by

$$T_2^{-1} = a^2 j(\bar{J})/(2\bar{J})^2$$

where $j(\bar{J})$ is the spectral density

$$j(\bar{J}) = {}^1/_2 \int_{-\infty}^{\infty} (J(0) - \bar{J})(J(t) - \bar{J}) \cos \bar{J}t \, \mathrm{d}t$$

The observation of an increase in the line width can therefore result from a decrease in $\bar{J}$ or an increase in the spectral density, $j(\bar{J})$, or both. As long as $\bar{J} \gg a$ it is impossible to distinguish between these alternatives. Since a change in the nature of the ionizable groups in I and II could affect both $\bar{J}$ and $j(\bar{J})$ it is not possible, as Ferruti, *et al.*,[1] have done, to ascribe the line-width differences to variations in $\bar{J}$ alone.

The spectrum of III at pH 2.6 resembles that of IV at 23° and an increase in pH to 10.8 results in a three-line spectrum similar to IV at −22°. The observation of three lines is consistent with a small value of $\bar{J}$ (in fact $\bar{J} \ll a$) and would suggest a dramatic change in the spin exchange. However, any value of $\bar{J}$ in the presence of extreme line broadening would also produce a three-line spectrum. Indeed, in the case of the glutarate, IV, the spectral changes shown in Figure 1 result predominantly from an increase in the line widths. The variation in the spectra of III observed by Ferruti, *et al.*, might be caused by a reduction in $\bar{J}$, but on the basis of their results an increase in $j(\bar{J})$ cannot be ignored. It is possible to distinguish between these two alternatives by measuring the intensities of the lines for solutions of known concentration.[3] The interpretation of biradical spectra measured in spin-labeled studies of nerve membranes suffers from similar errors.[4]

In conclusion we emphasize that caution must be exercised in the interpretation of the electron resonance spectra of flexible biradicals when the number of spectral lines may often be obscured by extreme line broadening.

Acknowledgments. We are grateful to the Science Research Council for a grant toward the cost of the spectrometer and to Consiglio Nazionale delle Ricerche of Italy for the award of a Fellowship to G. F. P.

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[3] H. Lemaire, A. Rassat, P. Rey, and G. R. Luckhurst, *ibid.*, **14**, 441 (1968).

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[5] On leave from Istituto di Chimica Organica e di Chimica Industriale, Bologna, Italy.

G. R. Luckhurst, G. F. Pedulli[5]
Department of Chemistry, The University
Southampton SO9 5NH, England
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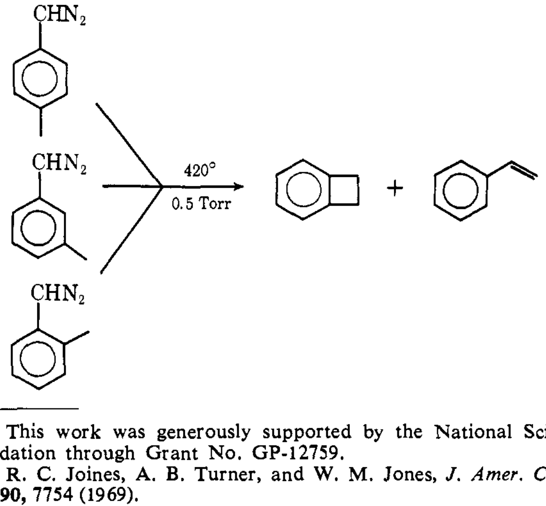
Interconversion of *o*-, *m*-, and *p*-Tolylcarbene[1]

Sir:

The rearrangement of phenylcarbene to cycloheptatrienylidene has recently been reported.[2] We describe here reactions which demonstrate the interconversion of substituted phenylcarbenes and their further rearrangement to methylphenylcarbene, and which suggest that the ring expansion of phenylcarbene to cycloheptatrienylidene is reversible.

The interconversion of substituted phenylcarbenes was demonstrated by constructing molecules incorporating a carbene trap at a remote position. The carbene can only react with the internal trap if rearrangements occur. The internal trap chosen was a methyl group and it was anticipated that should interconversion of the tolylcarbenes occur, products from *o*-tolylcarbene would be isolated no matter which of the three isomers was used as starting material. It was expected that *o*-tolylcarbene would be trapped as benzocyclobutene and that further rearrangement to methylphenylcarbene would be signaled by the appearance of styrene. The carbenes were generated in the gas phase by evaporating the corresponding diazo compound at 0.5 Torr through a 420° furnace into a trap cooled in a Dry Ice–acetone slurry. There can be little doubt that the initial species produced under these conditions is the unrearranged carbene.[3] Remarkably, it was found that generation of either *m*- or *p*-tolylcarbene under these conditions led to benzocyclobutene and styrene in the ratio 0.8.[4] The yield



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[1] This work was generously supported by the National Science Foundation through Grant No. GP-12759.

[2] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 7754 (1969).

[3] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 5; "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim/Bergstr., Germany, 1969.

[4] The yield was measured for the *para* case, but the *meta* is very similar. A number of trivial sources of the products have been eliminated. Thus the aldehydes from which the diazo compounds were made survive the reaction conditions unchanged and benzocyclobutene is not converted to styrene under the reaction conditions. Styrene is not isomerized in the flowing system at 350–600°.[5]