An Electron Spin Resonance Study of the Methyl- and Cyclopropyltropenyl Radicals and Dianion Radicals

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Abstract: The esr spectra of the cyclopropyl- and methyltropenyl radicals and dianion radicals have been measured, analyzed, and interpreted. In the dianion radicals the symmetrical tropenyl-like ABMO is occupied by the odd electron. HMO–McConnell calculations of the hyperfine splittings give excellent agreement with experiment without consideration of vibronic coupling. In the neutral radicals the odd electron occupies an orbital which is predominantly but not purely the antisymmetric tropenyl-like ABMO. Thermal and vibronic mechanisms for the mixing have been discussed and minimum electrical perturbations calculated for both substituents.

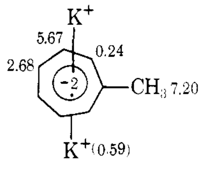
The tropenyl system (C_7H_7) is one of the most versatile of the π conjugated hydrocarbon systems.[1] The tropenylium ion (cation) is renowned for its impressive stability, the tropenyl radical exceptionally stable, and the tropenide ion (anion) stable enough to be readily preparable. For chemists interested in free radicals the system is even more fascinating. In addition to the neutral tropenyl radical already mentioned, the system smoothly forms a quite stable dianion radical having nine π electrons.[2,3] In all, four relatively stable tropenyl species are known. Despite much current interest in vibronically near-degenerate systems, not many substituted tropenyl radicals and no substituted tropenide dianion radicals have been investigated. A recent study of the *tert*-butyl- and 1,3,5-tri-*tert*-butyltropenyl (neutral) radicals deserves special mention.[4] The present work is concerned with the methyl- and cyclopropyltropenyl radicals and the corresponding dianion radicals. Some of the esr data to be discussed were tabulated without comment in a previous paper treating conformational analysis, in which only the substituent β hfs were of immediate interest.[5] Attention should also be drawn to revisions of some of the hfs as a result of later work.

Experimental Section

The syntheses and methods of generation of the radicals and dianion radicals have been described in detail elsewhere.[5] The dipotassium and disodium salts of methyltropenide were prepared by alkali metal reduction of the mixture of position isomers of the dimeric hydrocarbon in THF (sodium salt) or DME–THF (potassium salt). The cyclopropyl dianion radicals are quite unstable and were prepared by alkali metal reduction of the mixture of the position isomers of cyclopropyltropenyl methyl ether in 2-methyltetrahydrofuran at −130°. Cleavage of the cyclopropyl ring apparently occurs at about −100° and above.

The neutral radicals were generated in an esr cavity by thermolysis (190°) of the hydrocarbon dimers. These radicals were too unstable to afford useful temperature dependencies.

Results and Discussion



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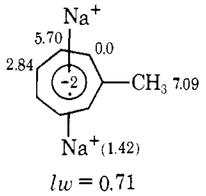
1



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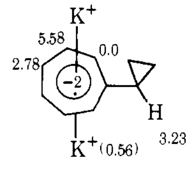
2



$lw = 0.32$

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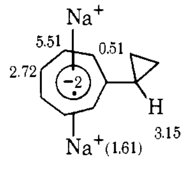

$lw = 0.24$

4

The assigned esr hfs (in gauss) are given alongside the appropriate position in structures **1**–**4**, below (lw = line width in gauss). All of the ring hfs arise from equivalent pairs of protons, and the metal hfs are also from equivalent pairs of metal ions, as befits a dianionic species. The sodium hfs of **2** and **4** are similar in magnitude to each other and to that observed for the parent tropenide dianion radical ($a_{2\mathrm{Na}^+}$ = 1.74).[2,3] Dipotassium tropenide did not exhibit a resolved potassium hfs, so that the potassium splittings found in **1** and **3** above are the first such hfs to be observed for a dianionic radical. Noteworthy and reassuring is the fact that dipotassium and disodium methyltropenide have very similar proton hfs as do the two salts of the cyclopropyltropenide dianion radical. Moreover, the cyclopropyltropenide spectra have ring hfs which are quite close to those in the methyltropenide case. The effective Q values for the latter, using the single proton equivalent of the methyl hfs, are 24.17 (sodium salt) and 24.38 (potassium salt), in excellent agreement with the value of 24.36 found for the parent dianion radical. The internal consistency of the data argue convincingly for their correctness. In addition, excellent agreement with theory will be demonstrated below.

That the cyclopropyl methine hfs is less than the methyl hfs has already been noted[5] and explained on the basis of a cyclopropyl preference for its "bisected" conformation, in which the methine proton lies in the nodal plane of the tropenyl system.

Theoretical values of the hfs of these dianion radicals have been calculated by the HMO and Pariser–Parr methods (the latter are in parentheses) and are given in

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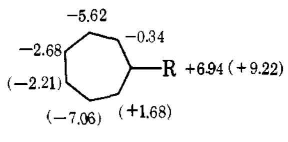
[1] A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 277.

[2] N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, **89**, 4390 (1965).

[3] N. L. Bauld and M. S. Brown, *ibid.*, **89**, 5417 (1967).

[4] G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968).

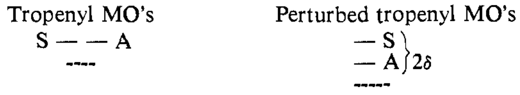
[5] N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *J. Amer. Chem. Soc.*, **91**, 6666 (1969).



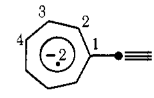
5

5. The odd electron is assumed to occupy a symmetrical tropenyl type ABMO ($E = \alpha - 0.44\beta$ in the HMO scheme). The spin densities calculated by each method were translated into hfs using a McConnell equation[6] with $Q = -24.36$, the value observed for the parent tropenide dianion radical. $Q = +24.36$ was used for the substituent β hfs. Note that the agreement with the HMO calculation is outstanding, that with the PP calculation only fair. In either case the agreement is good enough to support the basic assumption that it is the symmetrical tropenyl-type MO which is occupied by the odd electron in these dianion radicals. A view of this MO, in terms of spin density, is new for the tropenyl system. Indeed, the comparable orbital in other cyclic conjugated systems is not often accessible from the point of view of esr spectroscopy of electron occupancy. As depicted in Scheme I, the symmetrical MO is perturbed to a higher energy than its formerly codegenerate antisymmetric companion by an electron-donating substituent, such as an alkyl or cycloalkyl group. Only when the system can consume sufficient electrons to fill the A and then singly occupy the S molecular orbital is a spin distribution characteristic of the S molecular orbital observed (assuming the usual electron-donor substituent). For the more common and stable neutral systems having $4n + 2$ π electrons this requires the formation of a trianion radical, a species still unknown in the hydrocarbon series. However, $4n$ systems have the nearly degenerate pair at approximately the nonbonding level and one of the MO's is already filled in the neutral hydrocarbon. Consequently the S orbital is occupied at the readily accessible anion radical stage. On the other hand, $4n$ systems themselves are relatively unstable, and relatively few are available. The cyclooctatetraene anion radical, however, is an example of the aforementioned type.[7] In $4n + 1$ neutral systems, such as cyclopentadienyl, a tetraanion radical would be required for S occupancy. The dianion radicals of the present paper are members of the $4n - 1$ series, where the relevant pair of MO's is antibonding, but not powerfully so, and the required state of reduction is easily achieved by metal reduction. To summarize, S orbital occupancy can be expected for dianion radicals in the $4n - 1$ series of neutral hydrocarbons and in the anion radicals of such $4n$ systems as are available.

Scheme I

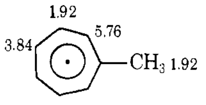


The splendid agreement of the experimental hfs with those expected for an odd electron occupying the symmetrical Hückel MO might indicate the absence of vibronic interaction between the S and A states, *i.e.*, the states wherein the odd electron occupies the S and A orbitals, respectively. A simple and tenable conclusion would be that methyl and cyclopropyl both represent sufficiently large perturbations as to minimize vibronic mixing, which is largest when the states are closest in energy. However, it is also conceivable that errors inherent in the HMO method (neglect of electron correlation) approximately nullify the effect of neglecting vibronic interaction in our purely electronic calculation. Such a cancellation is entirely plausible,[4,8] since vibronic mixing tends to even out the spin densities at all positions, whereas calculations, such as the PP one, which include electronic repulsions tend to exaggerate existing positional differences, predicting, for example, negative spin densities at some positions and enhanced positive ones at the others. The probability of the required coincidence is thus relatively high. Nevertheless, the initial conclusion, that the HMO tropenyl orbitals are valid and that vibronic interactions are small, is preferred on the basis of other results in the tropenyl system. The observed hfs in the propynyltropenyl dianion radical (**6**) are $a_2 = -6.99$, $a_3 = -1.00$, and $a_4 = -4.53$ with $a_{2K^+} = 0.49$ and $a_{CH_3} = 0$.[9] Here it is the virtually pure antisymmetrical Hückel MO that is actually occupied, as may be gathered from the fine agreement of the observed hfs with those predicted by a Hückel–McConnell calculation (−6.67, −1.07, and −4.25). In this system however, the perturbation is a conjugative and doubtlessly rather large one, so that vibronic interaction may safely be assumed negligible. At least in this case, then, vibronic interaction is not needed to produce agreement between observed hfs and HMO-calculated ones. Finally, it is pertinent to note that there is precedent for assuming methyl to represent a rather large perturbation, in the present sense, at least in comparison to *tert*-butyl.[4]



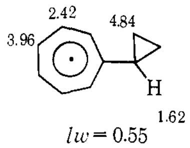
6

The experimental hfs of the two neutral radicals are listed in structures **7** and **8**. In addition, HMO–McConnell calculations are given in structure **9** for the case of single occupancy of the antisymmetrical tropenyl-type ABMO. A Q value of −25.34 was used for the ring hfs, this being the value observed for the parent tropenyl radical at this temperature. In contrast to the dianion radical results, the agreement is rather poor. Agreement can, however, be simulated by mixing in some of the S molecular orbital. In the cyclopropyl case about 27% and in the methyl case about 20% of the S orbital give reasonably good agreement. The "predictions" are then $a_1 = 1.95$, $a_2 = 5.09$, $a_3 = 2.57$, and $a_4 = 3.95$, and $a_1 = 1.44$, $a_2 = 5.54$, $a_3 = 2.25$, and $a_4 = 4.06$, respectively. For



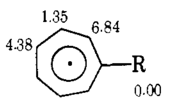
$lw = 0.81$

7



$lw = 0.55$

8



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(6) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
(7) A. Carrington and P. F. Todd, *Mol. Phys.*, **7**, 533 (1964).
(8) R. E. Moss, *ibid.*, **10**, 339 (1966).
(9) C. E. Hudson and N. L. Bauld, unpublished work.

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comparison, the *tert*-butyltropenyl radical has hfs of $a_2 = 4.39$, $a_3 = 2.71$, and $a_4 = 3.88$ at 173°.[4]

The observed mixing could, in theory, be either vibronic or thermal, or both in origin. Although it appears that vibronic coupling is relatively unimportant in the dianion radicals at low temperature, it does not necessarily follow that it is equally ineffectual in the neutral radical cases. If one does assume that mixing is purely a thermal equilibration between A and S states, the electrical perturbation, 2δ,[8] between the states is calculated to be 406 and 551 cal for the cyclopropyl and methyl cases, respectively. These figures would only be lower limits if vibronic coupling is important.

It is interesting that cyclopropyl engenders a smaller perturbation than methyl. It is possible to offer two plausible electronic explanations. First, it is expected that the nearly sp^2 hybridized cyclopropyl group will be less electron donating, inductively, than methyl. That part of the perturbation which is of inductive genesis will thus be smaller for cyclopropyl. Further, cyclopropyl is, to a greater extent than methyl, a conjugating group and, as has been seen, conjugation preferentially stabilizes the S orbital. The net destabilization of the S orbital by cyclopropyl is thus expected to be less than that by methyl.

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Vinyl Radicals. VII. Stereochemistry of the Free Radical Addition of Ethyl Mercaptan to Ethoxyacetylene. A 1-Alkoxyvinyl Radical

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Abstract: Preparative scale free radical additions of ethyl mercaptan to ethoxyacetylene give mixtures of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethenes (**1**). The stereochemistry of this addition was studied over an initial mercaptan concentration range of 1 *M* to 8×10^{-4} *M*. The lowest conversion sample in each case shows *cis*-**1**/*trans*-**1** > 100. The kinetically controlled addition, therefore, is stereospecific and trans. These results are discussed in terms of an intermediate *cis*-1-ethoxyvinyl radical which is formed stereospecifically and which has appreciable configurational stability.

We previously described the results of extended Hückel molecular orbital calculations of the energies of some plausible geometries of the 1-vinyl vinyl radical.[1] These results, in part, prompted us to propose a linear structure with the half-filled p orbital conjugated with the substituent π system as the preferred structure for the 1-vinyl and the related 1-phenyl vinyl radicals. This geometry provided a convenient rationalization[1] of the unusually stereoselective reactions of the 1,2-diphenyl vinyl radical.[2] Similar calculations[1] predict bent geometries for the vinyl and 1-methyl vinyl radicals; the former result is in agreement with many other calculations.[3] Our calculations also predict planar and pyramidal geometries for methyl[4] and trifluoromethyl[5] radicals, in accord with experiment. As part of the calculations, we compared the energies of bent and linear 1-substituted vinyl radicals as an estimate of the barriers to interconversion of isomeric, bent radicals. The vinyl and 1-methyl vinyl radicals both show[1] a small preference for bent geometries. This result is in accord with esr studies and chemical experiments which indicate that vinyl and 1-alkyl vinyl radicals are bent and that stereoisomeric radicals interconvert rapidly.[6] A more stimulating finding was that bent (120°) 1-hydroxy and 1-fluoro vinyl radicals calculate to be very much more stable than the linear forms (180°). The calculations, therefore, suggested[7] candidates for bent, configurationally stable vinyl radicals. This paper reports a study of the stereochemical capabilities of a 1-alkoxy vinyl radical obtained as an intermediate in the free radical addition of ethyl mercaptan to ethoxyacetylene.

Results

The free radical addition of ethyl mercaptan to 1 equiv of ethoxyacetylene in pentane gives a mixture of *cis*- and *trans*-1-ethoxy-2-(ethylthio)ethene (*cis*- and *trans*-**1**).[8] Each isomer was obtained in a high state of

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