minimal amount of variation. The rate constants obtained vary somewhat, and the question arises whether the amount of variation should be interpreted as indicating flaws in the method. We can only state an opinion at this time because too many unknowns still exist for us to advance a definitive proof. However, we have shown that the kinetic variations we observed are not unreasonable by comparison with such other gas-phase and condensed-phase data which exists, and thus we are of the opinion that the experimental method is valid and thus that the observed variations are real properties. If this really be the case (as only more extensive work can show), it is clear that the chemical ionization method is a sensitive one which will reflect and be useful for the determination of small variations in molecular properties.

Acknowledgment. We wish to acknowledge with thanks the gift by Esso Research and Engineering Co., Linden, N. J., of the Esso chemical physics mass spectrometer.

An Electron Spin Resonance Study of a Spirotetraene and a Spirodienone Radical Anion

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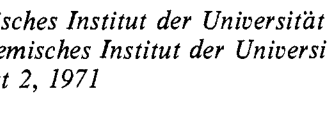
Contribution from Physikalisch-Chemisches Institut der Universität Basel, Basel, Switzerland, and Organisch-Chemisches Institut der Universität Zürich, Zürich, Switzerland. *Received August 2, 1971*

Abstract: Esr spectra of the radical anions obtained by electrolytic reduction of spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione (**1**) and spiro[5.5]undeca-1,4-dien-3-one (**2**) have been recorded and analyzed. The similarity in the hyperfine structures of two radical anions (large splittings by two protons only) points to an essential localization of the spin population on one dienone moiety in $\mathbf{1}^-$. This statement is substantiated by a simple HMO model. All-valence-electrons calculations account satisfactorily for the spin distribution in both $\mathbf{1}^-$ and $\mathbf{2}^-$, if a minute perturbation is applied to one of the oxygen atoms in $\mathbf{1}^-$. A reasonable assignment of the coupling constants to sets of equivalent protons could be based on the results of INDO calculations. This procedure also allows conclusions to be drawn about the mechanisms of spin transfer to hydrogen 1s orbitals. Although the singly occupied orbitals of $\mathbf{1}^-$ and $\mathbf{2}^-$ are essentially localized on one dienone moiety, the extent of delocalization over the spiro-carbon atom is considerable.

A theoretical treatment of spiroconjugation[2] has stimulated research in this field.[3-6] Although esr spectroscopy is a tool well suited to the study of π-electron delocalization in the radical ions of spiroconjugated compounds, to our knowledge, only one such study has been reported.[7] The observed spectrum of the radical anion of bis(2,2′-biphenylene)methane suggested that spin delocalization occurs over the two mutually perpendicular π systems; however, neither an analysis of the esr hyperfine structure nor a detailed discussion of the results was presented. It is noteworthy that spin delocalization over two formally orthogonal but not spiroconjugated π systems has been recently observed in the radical anion of 2,4,6,2′,4′,6′-hexa-*tert*-butylacetylene.[8]

A few years ago, spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione (**1**), a member of the class of compounds named "spirotetrenes," was synthesized.[3] Subsequently, a MO model of **1** was put forward, which is consistent with its electronic spectrum.[4]

In the present paper we wish to report an esr study of the radical anions of spirotetraene **1** and spiro[5.5]undeca-1,4-dien-3-one (**2**).[3]



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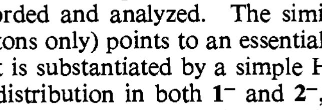

2

Preparations of the Radical Anions and Analysis of Their Esr Spectra

The radical anions, $\mathbf{1}^-$ and $\mathbf{2}^-$, were obtained upon electrolytic reduction of the parent compounds in a 1:1 mixture of *N*,*N*-dimethylformamide (DMF) and acetonitrile (ACN), with tetraethylammonium perchlorate as supporting salt. The use of this mixture instead of pure solvent (DMF or ACN) provided an extension of the temperature range (down to −90°) for the generation of the radical anions and the observation of their

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[1] (a) Universität Basel; (b) deceased January 1972; (c) Universität Zürich.

[2] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); R. Hoffmann, A. Imamura, and G. Zeiss, *ibid.*, **89**, 5215 (1967).

[3] G. Farges and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966).

[4] R. Boschi, A. S. Dreiding, and E. Heilbronner, *J. Amer. Chem. Soc.*, **92**, 123 (1970).

[5] G. Haas, P. B. Hubert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, **54**, 491 (1971).

[6] A. Gamba, G. F. Tantardini, and M. Simonetta, *Theor. Chim. Acta*, **20**, 12 (1971).

[7] R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

[8] H. E. Zimmerman and J. R. Dodd, *J. Amer. Chem. Soc.*, **92**, 6507 (1970).

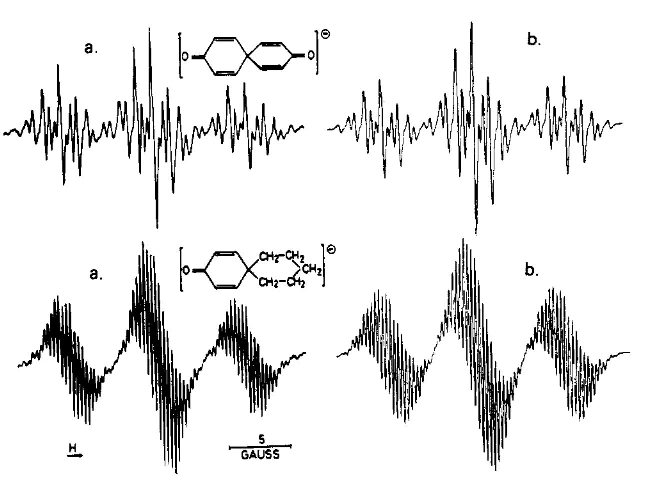


Figure 1. Esr spectra of the radical anions 1^- (top) and 2^- (bottom). (a) Experimental spectra: solvent, DMF-ACN (1:1); gegenion, $(C_2H_5)_4N^+$; temperature, −75 (1^-) and 0° (2^-). In the spectrum of 1^-, decay of the radical anion causes a decrease in the intensity from left to right. (b) Computer simulated spectra: line form, Lorentzian; line width, 0.20 (1^-) and 0.15 G (2^-). For coupling constants, see Table I.

esr spectra; such an extension is required by the instability of 1^- at higher temperature.[9] The spectra of 1^- and 2^- at −75 and 0°, respectively, are reproduced in Figure 1a.

Both spectra consist of three groups of lines due to a major splitting by two protons; the remaining protons give rise to minor splittings within each group. Analysis of the hyperfine structure results in the coupling constants listed in Table I and checked by a computer simulation of the spectra (Figure 1b).[10]

Table I. Coupling Constants of Protons in Radical Anions 1^- and 2^-

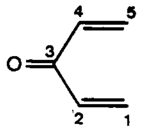
Radical anion	Temp, °C	Major splittings,[a] G	Minor splittings,[a] G
1^-	−75	7.62 ± 0.05 (two)	1.38 ± 0.02 (two)
			1.32 ± 0.02 (two)
			0.87 ± 0.01 (two)
2^-	0	7.50 ± 0.05 (one)	1.25 ± 0.05 (two)
		7.11 ± 0.05 (one)	0.94 ± 0.03 (four)
			0.62 ± 0.03 (two)
			0.25 ± 0.02 (two)

[a] Numbers of protons responsible for the splitting are given in parentheses.

Since no deuterated derivatives of 1^- and 2^- are at present available, the assignment of the coupling constants to individual protons in the two radical anions will be based on MO calculations. As demonstrated below, such models not only permit a reasonable assignment of the experimental data but are also helpful in the discussion of the spin distribution in 1^- and 2^-.

MO Calculations and Assignment of the Coupling Constants

π-Electron Model. 1,4-Pentadien-3-one (**3**) is the simplest model of **2** and of one dienone moiety in **1**.



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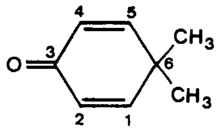

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HMO calculations for the radical anion 3^-, which make use of heteroatom parameters $\alpha_O = \alpha + \beta$ and $\beta_{CO} = 1.5\beta$, yield the values 0.268 and 0.053 for the π-spin populations at the 1,5 and 2,4 carbon atoms, respectively. The McLachlan treatment[11] modifies the larger number to 0.388 and the smaller one to −0.056, if the parameter λ is given its usual value of 1.2. By means of the McConnell relation[12] and the factor $Q_{CH} = -22.5$ G[13] one thus obtains the coupling constants of −8.77 and +1.26 G for the protons in the 1,5 and 2,4 positions, respectively. These numbers compare favorably with the recently published experimental data for the radical anion of 6,6-dimethylcyclohexa-1,4-dien-3-one (**4**), 7.08 and 1.14 G, where each value represents the coupling constant for a pair of equivalent protons.[14] The assignment required by theory, of the larger value to the protons in 1,5 positions and of the smaller to those in 2,4 positions, has been confirmed by the investigation of the 2-methyl derivative of 4^-.[14]

The π-spin populations, as predicted by the HMO model of 3^- and as verified by the esr study of 4^-, account surprisingly well for the main features of the spin distribution not only in 2^- but also in 1^-. An important result is thus obtained, which might have already been inferred from the similarity in the hyperfine structures of the two radical anions: *The spin population in* 1^- *is essentially localized on one dienone moiety.* This localization requires a formal differentiation of the mutually perpendicular π systems in the spirotetraene. In the following, the dienone moiety primarily containing the odd electron in 1^- is denoted "first," and the carbon atoms in it are numbered 1–5. As a consequence, numbers 6–10 remain for the carbon atoms in the "second" dienone moiety.

It is evident that the largest coupling constants listed for 1^- and 2^- in Table I can be unequivocally assigned to the protons in the positions 1,5. Whereas the two protons are equivalent in 1^- and exhibit an identical splitting of 7.62 G, they are nonequivalent in 2^- and give rise to different splittings of 7.50 and 7.11 G. Clearly, the difference of 0.39 G in the coupling constants of the two protons in 2^- is a result of their different chemical environment due to the chair conformation of the adjacent cyclohexane ring (see Figure 2). At the temperature of esr investigation (0°), the frequency of conformational interconversion must be

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(9) At room temperature, the electrolytic reduction of spirotetraene **1** in DMF yields a well-defined esr spectrum which has been analyzed in terms of the coupling constants: 8.78, 3.24, 2.34, and 0.23 G for one, one, two, and four protons, respectively. This spectrum cannot be ascribed to 1^- but must arise from a secondary electrolysis product, probably a radical formed by rehybridization of the spirocarbon atom and aromatization of one six-membered ring.

(10) In the case of 2^-, no attempt has been made to obtain a more exact agreement between the experimental and simulated spectra. Since the relative intensities of the hyperfine lines are extremely sensitive to slightest changes in the coupling constants and/or line width, the great amount of labor required to attain such an agreement is not justified by the insignificant improvements in the accuracy of the esr data.

(11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(12) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(13) The absolute value of Q_{CH} has been set equal to the total spectral spread of the benzene radical anion: T. R. Tuttle and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 5342 (1958).

(14) G. A. Russell and G. T. Stevenson, *ibid.*, **93**, 2432 (1971).

Table II. Calculated and Experimental Coupling Constants (in Gauss) of the Protons in the Radical Anions of Dienones **3** and **4**, Spirotetraene **1**, and Spirodienone **2**

	Radical anion						
Position	3^- McLachlan	4^- Esr[a]	1^- INDO	1^- Esr	2^- INDO[b]	2^- Esr	Mechanism of spin transfer[c]
1	−8.73	7.08	−7.96	7.62	−7.31	7.11	π–σ s pol
2	+1.26	1.14	+2.32	1.32	+1.86	0.94[d]	π–π and π–σ s pol
4	+1.26	1.14	+2.32	1.32	+2.02	0.94[d]	π–π and π–σ s pol
5	−8.73	7.08	−7.96	7.62	−7.96	7.50	π–σ s pol
6,10			−2.02	0.87	−2.82 (e)	1.25	π–σ s pol
6,10					+1.21 (a)	0.62	s del } long-range
7,9			+2.47	1.38	+1.71 (e)	0.94[d]	s del } coupling
7,9					−0.10 (a)	0.25	
8					−0.04 (e)	<0.10	
8					−0.15 (a)	<0.10	

[a] Reference 14. [b] (e) = equatorial; (a) = axial. [c] s pol = spin polarization; s del = spin delocalization. [d] Accidental degeneracy.

thus less than 10^6 sec^{-1} (=0.39 G × 2.8 MHz/G);[15] the rate of interconversion is presumably decreased by the large dienone substituent of the cyclohexane ring.

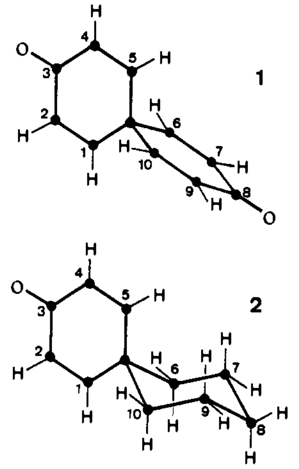
All-Valence-Electrons Models. Both extended Hückel (EH)[16] and INDO[17] calculations have been carried out for the radical anions 1^- and 2^-. The parameters used were taken from the original papers[16,17] and the interatomic distances based on data for related molecules.[18]

For the radical anion 1^- of ideal symmetry D_{2d}, the singly occupied orbital belongs to a degenerate pair. Since the experimental evidence requires an essential localization of the spin population on one dienone moiety, a perturbation must be introduced which reduces the symmetry and removes the orbital degeneracy. For reasons to be considered in the Discussion, an obvious choice for the perturbation is a slight modification of an energy parameter involved with one of the oxygen atoms. Such a perturbation, which has been applied in the EH and INDO calculations, meets the requirement of the experiment by leading to the localization of the spin population on one dienone moiety. A minute change in a geometrical parameter for one of the oxygen atoms has the same desired effect on the spin distribution. The result of the calculations is practically identical in view of the infinitesimal amounts of perturbation introduced in both models. On the other hand, it is interesting to note that no localization of the spin population occurs if, in order to achieve a chiral conformation advanced for **1** in a previous paper,[4] the dihedral angle between the two mutually perpendicular dienone moieties is slightly altered.

In the case of the radical anion 2^-, a frozen conformation has been adopted, in accordance with the different coupling constants of the protons in the positions 1 and 5. The pertinent molecular model of the spirodienone **2** is depicted in Figure 2, beneath that of spirotetraene **1**.

Figure 3 presents diagrams of the singly occupied orbitals as obtained for 1^- and 2^- by the INDO procedure. It is gratifying to note that, with one important exception to be discussed below, these diagrams comply with those resulting from the less sophisticated EH method.

Table II contains the proton coupling constants calculated by the INDO procedure, along with the McLachlan values for 3^- and experimental data for 1^-, 2^-, and 4^-. A factor Q_H = +504 G[19] was used to convert the 1s-spin populations at the hydrogen atoms into the coupling constants.



1

2

Figure 2. Molecular models of **1** and **2**.

There is reasonable agreement between the experimental and the calculated values, and the assignment made in Table II has been based on their optimal correlation. Interestingly, the INDO procedure yields too large absolute values for all coupling constants of substantial magnitude. On the other hand, the signs are likely to be correct and may be used as indicators of the major mechanism which gives rise to the pertinent 1s-spin populations (see Discussion).

The INDO calculations permit, *inter alia*, to specify the data for the two slightly nonequivalent protons in positions 1,5 of 2^-. According to the result of these calculations, the larger coupling constant should be assigned to that proton which is situated above the cyclohexane ring, *i.e.*, in the position denoted 5 in Figure 2. The fact that the expected nonequivalence of the two protons in positions 2,4 of 2^- is not found experimen-

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(15) No significant changes in the esr spectra have been observed on warming the solution to +40°, *i.e.*, to the highest temperature admissible by the stability of the radical anion 2^-.

(16) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2745 (1964). A Slater exponent of 1.3 was used for hydrogen atoms.

(17) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(18) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. **11** (1958).

(19) This Q_H value is identical with the coupling constant of the proton in the hydrogen atom: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

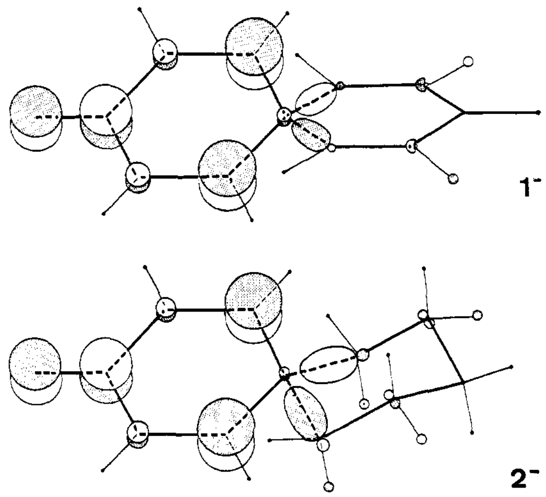

Figure 3. Schematic representations of the singly occupied orbitals in the radical anions 1^- and 2^-. The areas are proportional to the squares of the LCAO coefficients. Blank and dotted areas symbolize different signs.

tally may be explained by the relatively small difference in the coupling constants of such protons which are farther away from the cyclohexane ring than those in positions 1,5.

One may notice that the equatorial protons at the carbon atoms 6,10 and 7,9 of 2^- have coupling constants listed in the same row of Table II as the corresponding protons in the second dienone moiety of 1^-. Consideration of molecular models (Figure 2) makes it evident that the two sets of protons are similarly located with regard to the 1,5 carbon $2p_z$ orbitals bearing the bulk of the spin population. The INDO values calculated for these two sets exhibit a remarkable parallelism.

Discussion

Spin Localization. The observation that the spin population of 1^- is mostly localized on the first dienone moiety implies a "slow" rate of electron transfer to the second moiety. Under experimental conditions (solvent, DMF-ACN (1:1) mixture; gegenion, $(C_2H_5)_4N^+$; temperature range, -50 to $-90°$), this rate is estimated to be less than 2.8 MHz/G times the differences in the coupling constants of the protons in the two moieties, *i.e.*, less than 10^6–10^7 sec^{-1}.

The localization of the spin population on one dienone moiety can be readily rationalized by the assumption that the interaction of one of the oxygen atoms with the gegenion (and/or the solvent)[20] is sufficiently long-lived on the esr time scale. Such an interpretation is supported by MO models, in which a perturbation applied to one of the oxygen atoms indeed leads to the required localization of the spin population (see above).

The diagrams of the singly occupied orbitals shown in Figure 3 exhibit very similar patterns for 1^- and 2^-. Surprisingly, this is even true for the second dienone moiety of 1^- and the cyclohexane ring of 2^- despite their structural differences. Although in both radical anions, the orbitals are essentially localized on one dienone π system, the extent of delocalization over the spirocarbon atom is considerable. The LCAO coefficients have substantial magnitudes at the adjacent carbon atoms (6,10) and become extremely small only at the more remote ones (7,9 and 8).

The extent of delocalization over the spirocarbon atom and the similar pattern predicted by the MO models for the singly occupied orbitals of 1^- and 2^- are fully consistent with the main features of the spin distribution in the two radical anions.

Mechanism of Spin Transfer. In π-electron radicals two mechanisms are responsible for the presence of 1s-spin populations at hydrogens atoms:[21] the *direct* mechanism or *spin delocalization* and the *indirect* mechanism or *spin polarization*.

It is obvious that only the indirect mechanism provides hydrogen spin populations in the planar dienone π systems of 1^- (first moiety) and 2^- which primarily contain the odd electron. Whereas π–σ-spin polarization alone accounts for the largest and negative coupling constants of the protons in positions 1,5, both π–π and π–σ-spin polarizations must be invoked to rationalize the smaller and positive values for the protons in positions 2,4.

More problematic is the spin transfer to the hydrogen 1s orbitals in the second dienone moiety of 1^- and in the cyclohexane ring of 2^-, since now the direct mechanism must be considered as well. π–σ-spin polarization should still be mainly responsible for the negative coupling constants of the protons in positions 6,10 of 1^- and of the corresponding equatorial protons of 2^-. The prevalence of the indirect mechanism in this case is not surprising, since, as mentioned above, the singly occupied orbitals of 1^- and 2^- exhibit considerable populations at the adjacent carbon atoms (see Figure 3). On the other hand, the analogous populations at the carbon atoms 7,9 are vanishingly small, so that π–σ-spin polarization should play only a minor role in the spin transfer to the 1s orbitals of the adjacent hydrogen atoms. In fact, the positive sign of the coupling constants calculated for the protons in positions 7,9 of 1^- and the corresponding equatorial protons of 2^- gives evidence that these values are mainly due to the direct mechanism (spin delocalization). The location of the two pairs of protons with regard to the 1,5 carbon $2p_z$ orbitals is known to represent one of the most effective arrangements for long-range interaction.[22]

Of the remaining protons in 2^-, only the axial ones in position 6,10 have a coupling constant of a substantial magnitude. The positive sign of this coupling constant points to a direct mechanism of spin transfer. As shown by a molecular model, the two axial protons are arranged in a W-shape relative to the 1,5 carbon $2p_z$ orbitals and considerable empirical evidence from esr[23]

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(20) An interaction of this kind has been advanced to account for the nonequivalence of the two nitro groups in electrolytically generated radical anions of dinitrobenzenes (solvent DMF; gegenion, $(n\text{-}C_3H_7)_4N^+$; temperature range, -50–$+50°$): J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 699 (1964).

(21) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967; P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, London, 1967; K. Scheffler and H. B. Stegmann, "Elektronenspinresonanz," Springer-Verlag, Berlin, 1970; F. Gerson, "High Resolution ESR Spectroscopy," Verlag-Chemie, Weinheim/Bergstr., and Wiley, New York, N. Y., 1970.

(22) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(23) G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968.

and [illegible]r[24] studies indicates that such an arrangement is also very effective for long-range coupling.

The above suggestions for the main mechanism of spin transfer to the hydrogen 1s orbitals are summarized in the last column of Table II for all coupling constants of substantial magnitude (>0.5 G).

It is noteworthy that, in contrast to the hydrogen 1s-spin populations which arise by an indirect mechanism, those which are mainly due to a direct spin transfer must be already apparent in the one-orbital presentation and thus should be correctly predicted by the EH method as well. This is the case for the hydrogens in the positions 7,9 of $\mathbf{1}^-$ and the corresponding equatorial hydrogens of $\mathbf{2}^-$. However, the EH method fails to predict an appreciable 1s-spin population for the axial hydrogens in positions 6,10 of $\mathbf{2}^-$. It is difficult to give reasons for this disagreement between the INDO and EH procedures so long as the nature of the W-shape interaction is open to discussion.[25]

Furthermore, it is interesting to note that the equatorial and axial hydrogens in the positions 6,10 of $\mathbf{2}^-$ are linked to the dienone π system by the same number of sp^3-hybridized carbon atoms as the hydrogens in the freely rotating methyl groups of $\mathbf{4}^-$. A comparison of the mechanism responsible for the spin transfer to these hydrogens in the two radical anions is therefore indicated. Since the coupling constant of the methyl protons in $\mathbf{4}^-$ is surprisingly small (<0.06 G), Russell and Stevenson[14] suggested that the contributions of both the direct and indirect mechanisms are important and cancel each other in this case. The results of the present INDO calculations which predict different signs for the coupling constants of the equatorial and axial protons in the positions 6,10 of $\mathbf{2}^-$ are fully consistent with such an interpretation.

Orbital Mixing. As a final point, the possibility of "orbital mixing"[26] on the spin distribution in $\mathbf{1}^-$ will be briefly discussed. Since a perturbation is required to remove the degeneracy of the lowest antibonding orbitals in this molecule, the resulting energy gap depends on the amount of the applied perturbation. If the perturbation is slight, the gap will remain small and the two orbitals will be near-degenerate. Consequently the treatment of the spin distribution in $\mathbf{1}^-$ solely in terms of the more stable orbital might not be appropriate, because its less stable counterpart could make a significant contribution.

Since the two near-degenerate orbitals of $\mathbf{1}^-$ are essentially localized on different dienone moieties, an admixture of the less stable orbital would mainly affect the spin distribution in the second moiety. As a result, the $2p_z$-spin population in this moiety of $\mathbf{1}^-$ would be markedly different from those in the cyclohexane ring of $\mathbf{2}^-$, despite the similarity of the singly occupied orbitals predicted for the two radical anions. However, the experimental data for $\mathbf{1}^-$ and $\mathbf{2}^-$ do not exhibit such a difference and thus the spin distribution in $\mathbf{1}^-$ can be satisfactorily rationalized without invoking significant orbital mixing.

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[24] L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, Chapter 4-4.G.

[25] M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969); M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969); M. Barfield, *ibid.*, **93**, 1066 (1971), and other references therein.

[26] A. Carrington, *Roy. Inst. Chem. Lect. Ser.*, *1964*, 1 (3) (1965); W. D. Hobey, *J. Chem. Phys.*, **43**, 2187 (1965); E. de Boer and J. P. Colpa, *J. Phys. Chem.*, **71**, 21 (1967).