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# Unrestricted Hartree-Fock Calculation of Spin Distributions in Some Radical Anions Exhibiting Restricted Rotation about a Carbon Carbon Bond

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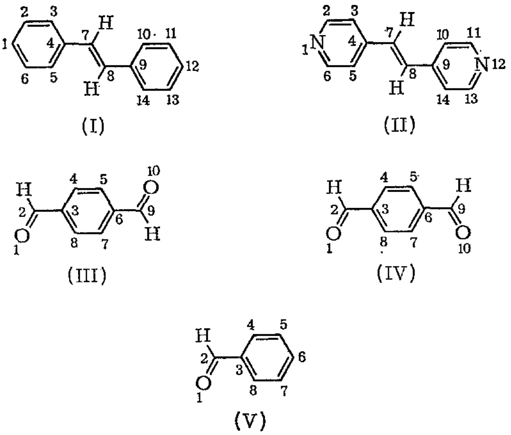
In the radical anions of trans-stilbene, trans-1,2-bis(4-pyridyl)-ethylene, cis and trans-terephthalaldehyde and benzaldehyde it has been found earlier by ESR experiments that the two ortho protons, as well as the two meta protons of the six-membered ring are not equivalent. We have made a systematic study of spin distributions in these systems by employing the UHF (Unrestricted Hartree Fock) and UHFAA (UHF incorporating the annihilation of the quartet spin component) methods. Satisfactory agreement with the experimental results has been obtained within the framework of these theories and without invoking the so called "$\alpha$ effect" or "$\beta$ effect".

Bei früheren ESR-Untersuchungen an *trans*-Stilben, *trans*-Dipyridyläthylen, Terephthalaldehyd und Benzaldehyd wurde gefunden, daß sowohl die *ortho*- wie die *meta*-ständigen Ringprotonen nicht gleichwertig sind. Wir haben die Spindichten in diesen Systemen mit der UHF- und der UHFAA-Methode untersucht. Befriedigende Übereinstimmung mit experimentellen Ergebnissen wurde erzielt, ohne daß dazu der sogenante $\alpha$- oder $\beta$-Effekt herangezogen werden mußte.

Dans les anions radicalaires du trans-stilbène, du trans-1,2-bis(4-pyridyl)-éthylène, des aldéhydes térephtaliques cis et trans, et de l'aldéhyde benzo'que, des expériences de r.p.e avaient montré que les deux protons en méta n'étaient pas équivalents. Nous avons effectué une étude systématique des distributions de spin dans ces systèmes en utilisant les méthodes U.H.F. (Hartree-Fock sans restriction) et U.H.F.A.A. (U.H.F. comportant l'annihilation de la composante quartet de spin). On a obtenu un accord satisfaisant avec les résultats expérimentaux dans le cadre de ces théories sans faire appel à de soi-disants effects $\alpha$ ou $\beta$.

## Introduction

Electron spin resonance studies of the radical anions of trans-stilbene (I), trans-1,2-bis(4-pyridyl) ethylene (II), trans-terephthalaldehyde (III), cis-terephthalaldehyde (IV) and benzaldehyde (V) have been made earlier [9, 20, 21]. It has been found that the isotropic coupling constants of the protons at the two ortho positions in the six-membered ring differ from each other. The same is true for the two meta protons also. This inequality arises from the presence of restricted rotation around a carbon carbon bond within these systems. Since resonance integrals between any two non-bonded atoms are not taken into account in the usual Hückel Molecular Orbital (HMO) calculation [22], these differences in the proton coupling cannot be predicted from a spin density calculation [12] made within this framework. However, these experimental asymmetries can be brought about by introducing artifacts like the so called "$\alpha$ effect" and/or "$\beta$ effect" [2, 9, 20, 21]. The validity of "$\alpha$ effect" and "$\beta$ effect" has been questioned earlier by Chang



(I) (II) (III) (IV) (V)

Fig. 1. Topology and numbering in trans-stilbene (I), trans-1,2-bis(4-pyridyl)-ethylene (II), trans-terephthalaldehyde (III), cis-terephthalaldehyde (IV) and benzaldehyde (V)

and Johnson [9]. These authors have shown the lack of even internal selfconsistency in these procedures. Furthermore in the radical anions of cis and trans-terephthalaldehyde, although these two procedures (namely "$\alpha$ effect "and "$\beta$ effect") predict the magnitude of the coupling constant equally well, their assignments are completely different from each other [21]. One might reasonably hope that procedures which take geometry explicitly into account and also include interelectronic terms might successfully predict the experimental asymmetry. Although these factors are considered in the restricted Hartree-Fock method [1, 18] it is not suitable because this procedure cannot yield negative spin density values; (they are expected in some of the systems described here [2]). More sophisticated procedures that can yield negative spin density values are the configuration interaction method [5, 7] and the UHF (Unrestricted Hartree-Fock) [19] and UHFAA (UHF incorporating the annihilation of quartet spin component) [19] methods.

Morokuma et al. [13] have studied the cis- and trans-terephthalaldehyde systems by a sophisticated MO method. But their assignments are in disagreement with experiment [21]. Recently Morokuma et al. [14] have also employed the UHF procedure of Brickstock and Pople [4] on the trans-stilbene radical anion. But agreement with experimental data is not very good particularly for positions having low spin density values; also their wave function is not a true eigenfunction of $S^2$ [19]. To our knowledge a systematic study of the spin distributions in these systems using UHF and UHFAA has not yet been reported. In view of these facts we started a program for the systematic study of spin distributions in a few systems exhibiting restricted rotation about a carbon-bond by employing both UHF and UHFAA procedures. The results of our study are given in this paper.

## Method of Calculation

Details of the method are not given here since the procedure is very well documented [19]. All systems studied here were taken to be planar. Geometry needed for trans-stilbene was taken from the literature [17]. For the sake of simplicity similar geometry was also assumed for trans-1,2-bis(4-pyridyl)-ethylene. For benzaldehyde and cis- and trans-terephthalaldehyde the bond lengths in the benzene ring were taken to be 1.39 Å. The carbon-oxygen bond length was taken to be 1.22 Å and the bond joining the aldehyde group to the benzene ring was taken to be 1.46 Å [8]. Valence state ionization potentials ($W_i$) and electron affinities ($A_i$) needed for the computation of one-centre two electron repulsion integrals were taken from the work of HINZE and JAFFÉ [6]. Two-centre two electron repulsion integrals were obtained following the procedure of PARISER and PARR [15]. Resonance integrals for various bonds were obtained by employing Kon's relation [10]. Approximate density matrices needed for the SCF iteration

Table. *Calculated and experimental splitting constants in the radical anions of trans-stilbene, trans-1,2-bis(4-pyridyl) ethylene, cis- and trans-terephthalaldehyde and benzaldehyde (in Gauss)*

| System | Position | Calculated Coupling Constants | | | Experimental[c] coupling constants | Coupling constants[d] calculated from Eq. (1) |
|---|---|---|---|---|---|---|
| | | Earlier[a] work | UHF[b] | UHFAA[b] | | |
| I | 1,12 | −3.93 | −4.55 | −2.97 | −3.89 | −3.61 |
| | 2,13 | +1.46 | +1.83 | +0.43 | +0.81 | +0.79 |
| | 3,14 | −2.63 | −3.08 | −2.02 | −2.96 | −2.37 |
| | 5,10 | −2.77 | −2.88 | −1.91 | −1.90 | −2.21 |
| | 6,11 | +1.51 | +1.66 | +0.32 | +0.30 | +0.67 |
| | 7,8 | −4.44 | −4.10 | −4.27 | −4.37 | −4.55 |
| II | 1,12 | | −3.99 | −2.68 | −2.50 | −3.01 |
| | 2,13 | | +0.27 | −0.52 | −0.25 | −0.31 |
| | 3,14 | | −1.46 | −1.16 | −2.14 | −1.30 |
| | 5,10 | | −1.40 | −1.15 | −1.80 | −1.27 |
| | 6,11 | | +0.07 | −0.66 | −0.35 | −0.45 |
| | 7,8 | | −3.05 | −3.31 | −4.25 | −3.41 |
| III | 2,9 | −4.90 | −3.87 | −4.10 | −3.89 | −3.45 |
| | 4,7 | −1.66 | −2.01 | −2.07 | −2.08 | −2.15 |
| | 5,8 | −1.22 | +0.21 | −0.68 | −0.70 | −0.45 |
| IV | 2,9 | −4.88 | −3.84 | −4.09 | −3.81 | −3.44 |
| | 4,5 | −1.06 | −0.52 | −1.08 | −1.16 | −0.97 |
| | 7,8 | −1.89 | −1.29 | −1.66 | −1.54 | −1.58 |
| V | 2 | | −9.16 | −9.27 | −8.57 | −8.55 |
| | 4 | | −4.79 | −3.44 | −4.69 | −3.98 |
| | 5 | | +2.84 | +0.75 | +1.31 | +1.30 |
| | 6 | | −6.39 | −4.54 | −6.47 | −5.47 |
| | 7 | | +1.62 | +0.05 | +0.75 | +0.45 |
| | 8 | | −3.47 | −2.51 | −3.39 | −2.78 |

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[a] Obtained from Refs. [*13*] and [*14*]. Results obtained by invoking "α effect" or "β effect" have not been included.

[b] Proton coupling canstant ($a_r$) were obtained by taking the relation $a_r = -27\,\varrho_r - 12.8\,(1 - P_r)\,\varrho_r$ where $\varrho_r$ and $P_r$ are respectively spin and electron density on atom $r$ (see Ref. [*19*]). Nitrogen coupling constant ($a_N$) was obtained by employing the relation $a_N = -21\,\varrho_N$ (see Ref. [*5*]).

[c] Data were taken from Ref. [*9, 20, 21*]. Assignments have been made on the basis of our present calculations.

[d] Coupling constants were calculated by using the relation $a_r = -27\,\varrho_r$ (see Ref. [*19*]) and using $\varrho_r$ obtained from Eq. (1) of text.

procedure were obtained from simple HMO wave functions and the various coulomb and resonance integrals needed for hetero-atoms were taken from STREITWIESER [32]. The topology and numbering used for these systems in the present work are given in Fig. 1 and our results on these systems obtained by UHF and UHFAA methods are given in the Table.

## Results and Discussion

### *Radical Anion of Trans-stilbene (I)*

For the trans-stilbene radical anion there is very little ambiguity in the choice of parameters and so it is an ideal system for the comparison of calculated spin densities with experimental results. We have done three different sets of calculations for this molecule. In the first calculation the parameters used were obtained by the procedure mentioned earlier in this paper. In the second set of calculations we used the parameters of BEVERIDGE and JAFFÉ [3] who recently discussed the UV spectrum of the trans-stilbene molecule. In the third set of calculations we have used the same set of parameters as in the first set of calculations, but here the resonance integrals between any two non-bonded atoms separated by less than 3 Å were included. For this purpose we employed Kon's relation [10] for the dependence of the resonance integral on the distance. Results of all these calculations predict essentially similar assignments. Hence, the results of the first set of calculations only are given in the table. It can be seen from this table, that our present assignment is different from that made by MOROKUMA et al. [14] and that the coupling constants obtained by MOROKUMA et al. are not in very good agreement with experiment, particularly for positions having low spin density values. This may be due to the fact that the wave function employed by them is not a true eigenfunction of $S^2$ [19, 16]. Comparing our UHF and UHFAA results it can be seen that UHFAA is better than UHF. Experimentally the largest coupling constant has been assigned to the 7,8-positions in trans-stilbene (Fig. 1) and UHFAA predicts this correctly but not UHF. The UHF results for positions having low spin density values are seen to be rather unsatisfactory in this case.

It has been observed earlier [11, 19] that if the single-excitation doublet is degenerate with the single-excitation quartet component then the unprojected spin density values would be better than the ones obtained after annihilation of the quartet spin component. On the other hand, if the single-excitation quartet component is degenerate with the restricted doublet part then the reverse would be true. It has also been further observed by SNYDER and AMOS [19] that conjugate hydrocarbon radicals approximate the second case. In view of these facts we favour the assignment made on the basis of our present UHFAA calculations over that made by MOROKUMA et al. [14].

### *Radical Anion of Trans-1,2-bis(4-pyridyl)-ethylene (II)*

Calculations were made for this radical anion of (II) by employing the parameters obtained as outlined earlier. The agreement with experiment seems to be fairly good. Here, UHFAA result appeared to be definitely better than UHF. A similar observation was also made earlier [16] for the radical anion of other aza-aromatics. In the present calculations both UHF and UHFAA results give essentially similar assignments for various coupling constants except for the fact that spin density values predicted by the UHF method for 2 and 6 positions are negative, while the UHFAA method predicts those to be positive. Unfortunately experimental data regarding the signs of the spin density values are not available. Since UHFAA has yielded generally more reliable results earlier [16] in other aza-aromatic radical anions and since here also it gives better overall agreement with experiment as compared to UHF, we have favoured the assignment based on UHFAA results over that given by UHF.

### *Radical Anions of Trans- and Cis-terephthalaldehyde (III and IV respectively)*

Parameters needed for the calculations were obtained as outlined previously in this paper. For these two radical anions, the UHFAA result is in excellent agreement with experiment. Both UHF and UHFAA predict the largest coupling constant in each of these two systems to be that for the aldehydic proton and this has been indeed confirmed by experiment [21]. It can be seen from the table, that our present results are much better than those obtained by MOROKUMA et al. [13]. It may be pointed out here that by invoking the so called "$\alpha$ effect" and "$\beta$ effect" apparently satisfactory agreement with experiment was shown earlier [21] for these two molecules. However, since these two prescriptions predict different assignments for the ring protons our present results based on UHF and UHFAA procedures are more reliable. Here again, UHFAA results for these two systems appear to be in better agreement with experiment in comparison to UHF results.

### *Radical Anion of Benzaldehyde (V)*

It can be seen from the table that for the benzaldehyde radical anion both UHFAA and UHF methods predict similar assignments. However, it is of interest to find that the UHF result is better than the UHFAA result, except for positions having low spin density values. Parameters used in the calculations were the same as those used for the computation of spin density values in cis and trans-terephthalaldehyde radical anions. It may be recalled that the UHFAA results for cis and trans-terephthalaldehyde radical anions were found to be definitely better than those obtained by UHF and the agreement with experiment was excellent. In view of these facts we feel that the benzaldehyde radical anion probably belongs to the category where the single-excitation doublet is degenerate with the single-excitation quartet component. Under these conditions the unprojected spin density will appear to be better than that obtained after annihilation [11, 19]. In our calculations for the benzaldehyde radical anion we have also varied $\delta_{W_O}$ (i.e. $W_O - W_C$) over a reasonable range ($-4.0$ eV to $-8.5$ eV) and have found that the UHF result is always better than the UHFAA result. When a similar variation was made in the case of the trans- and cis-terephthalaldehyde radical anions it was found that the UHFAA results were always better than UHF results. These observations indicate that the choice of the particular $\delta_{W_O}$ value is not responsible for making UHF results better than UHFAA results in the case of the benzaldehyde radical anion and vice versa in the case of the cis- and trans-terephthalaldehyde radical anions.

It has been suggested by SNYDER and AMOS [19] that the correct spin density can be obtained in the most general way by taking a proper linear combination of

UHF and UHFAA spin densities and the coefficients in the linear combination can be obtained if values of $E^{rf}$, $E^{se}_{3/2}$ and $E^{se}_{1/2}$ are available (the notations used here are those of Ref. [19]). However, in the present work we have taken recourse to a more approximate way to find this linear combination. Following Snyder and Amos [19] we can write

$$\varrho_{\mathrm{EHF}} \sim (3\varrho_{\mathrm{UHFAA}} + \varrho_{\mathrm{UHF}})/4 \tag{1}$$

where $\varrho_{\mathrm{EHF}}$, $\varrho_{\mathrm{UHFAA}}$, and $\varrho_{\mathrm{UHF}}$ are spin density values for the $r^{th}$ position using extended Hartree-Fock, UHFAA and UHF formalisms, respectively. Using the spin density obtained from Eq. (1) coupling constants were calculated for the systems I to V. The results are given in last column of the Table and appear to be in good agreement with experiment.

## Conclusion

Using sophisticated methods like UHF and UHFAA we have been able to make unambiguous assignments of various hyperfine splitting constants in some radical anions exhibiting restricted rotation about a carbon carbon bond. Our results point to the conclusion that both UHF and UHFAA spin density values are needed for making reliable assignments though in most cases investigated so far UHFAA results alone suffice.

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