A Semiempirical Unrestricted SCF Calculation of the *trans*-Stilbene Anion Radical

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In recent electron spin resonance studies of the anion radicals of *trans*-stilbene,(1) azobenzene,(2) benzaldehyde and acetophenone,(3) it has been found that the isotropic coupling constants of the protons of two *ortho*-positions, and also that of two *meta*-positions in the phenyl ring, differ from each other. These differences can not be interpreted by either the Hückel molecular orbital (HMO) method or the McLachlan procedure,(4) because in these methods the resonance integrals between non-bonded atoms are not taken into account.

Hence, we will make an semiempirical unrestricted SCF calculation, as proposed by Pople and Nesbet(5) and developed by Brickstock and Pople,(6) for the *trans*-stilbene anion radical. It will be shown in the present treatment that the difference between spin densities at two *ortho*-positions and also that at two *meta*-positions appear in accordance with the experimental results.

The Method of Calculation

In the semiempirical unrestricted SCF method, two sets of LCAO coefficients, $\chi_{i\mu}{}^{\alpha}$ and $\chi_{i\mu}{}^{\beta}$, are calculated as follows:

$$\sum_{\nu} F^{\alpha}_{\mu\nu}\chi^{\alpha}_{i\nu} = E^{\alpha}_{i}\chi^{\alpha}_{i\mu};\ \sum_{\nu} F^{\beta}_{\mu\nu}\chi^{\beta}_{i\nu} = E^{\beta}_{i}\chi^{\beta}_{i\mu} \qquad (1)$$

where:

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1) R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **41**, 3272 (1964).

2) E. T. Strom, G. A. Russell and R. Konaka, ibid., **42**, 2033 (1865).

3) N. Steinberger and G. K. Fraenkel, ibid., **40**, 723 (1960).

4) A. D. McLachlan, *Mol. Phys.*, **2**, 233 (1960).

5) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

6) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

TABLE I. CALCULATED AND EXPERIMENTALLY FOUND[1] SPIN DISTRIBUTIONS IN THE *trans*-STILBENE ANION RADICAL

Position	a_H[a]	$\lvert\rho_{\exp}\rvert$[9]	ρ_{SCF}	$\rho_{McL.}$	ρ_{HMO}
1	2.90	0.132	+0.1230	+0.1232	+0.0750
2	0.81	0.036	−0.0672	−0.0804	+0.0063
3	3.89	0.173	+0.1747	+0.1436	+0.0984
4	0.30	0.013	−0.0651	−0.0804	+0.0063
5	1.90	0.0844	+0.1168	+0.1232	+0.0750
6	—	—	+0.0205	−0.0031	+0.0472
7	4.37	0.194	+0.1974	+0.2739	+0.1919

a) From Ref. 1), in units of gauss. The assignment of the coupling constants of two sets of *orth*-protons and of *meta*-protons is made based on our calculation.

$$\left.\begin{aligned}
F^{\alpha}_{\mu\mu} &= U_{\mu\mu} + P^{\beta}_{\mu\mu}\gamma_{\mu\mu} + \sum_{\sigma(\neq\mu)}(P_{\sigma\sigma}-1)\gamma_{\mu\sigma}\\
F^{\beta}_{\mu\mu} &= U_{\mu\mu} + P^{\alpha}_{\mu\mu}\gamma_{\mu\mu} + \sum_{\sigma(\neq\mu)}(P_{\sigma\sigma}-1)\gamma_{\mu\sigma}\\
F^{\alpha}_{\mu\nu} &= \beta_{\mu\nu} - P^{\alpha}_{\nu\nu}\gamma_{\mu\nu}\ (\mu\neq\nu)\\
F^{\beta}_{\mu\nu} &= \beta_{\mu\nu} - P^{\beta}_{\mu\nu}\gamma_{\mu\nu}\ (\mu\neq\nu)
\end{aligned}\right\} \qquad (2)$$

$$\left.\begin{aligned}
P^{\alpha}_{\mu\nu} &= \sum_{i}^{\mathrm{occ}}\chi^{\alpha}_{i\mu}\chi^{\alpha}_{i\nu};\ P^{\beta}_{\mu\nu} = \sum_{i}^{\mathrm{occ}}\chi^{\beta}_{i\mu}\chi^{\beta}_{i\nu}\\
P_{\mu\nu} &= P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}
\end{aligned}\right\} \qquad (3)$$

In Eq. 1, 2 and 3, all the notations are the same as Brickstock and Pople's.[6] The spin density at the carbon atom μ, ρ_{μ}, is obtained from Eq. 4:

$$\rho_{\mu} = P^{\alpha}_{\mu\mu} - P^{\beta}_{\mu\mu} \qquad (4)$$

As the penetration integral is neglected, $U_{\mu\mu}$ becomes a constant over all the carbon atoms. $\gamma_{\mu\nu}$ is calculated by means of the approximation of Pariser and Parr.[7] The resonance integral, $\beta_{\mu\nu}$, is calculated by means of Eq. 5:

$$\beta_{\mu\nu} = \begin{cases} -10.44\, S_{\mu\nu}\ \mathrm{eV.} & (R_{\mu\nu} < 3.0\text{Å})\\ 0 & (R_{\mu\nu} \geqq 3.0\text{Å}) \end{cases} \qquad (5)$$

where $R_{\mu\nu}$ is the distance between the μth and νth atoms, and $S_{\mu\nu}$ is the overlap between two $2P_Z$ Slater-type atomic orbitals with $Z^* = 3.25$.

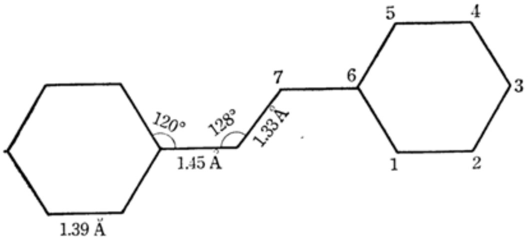

Fig. 1. Structure and numbering of positions of *trans*-stilbene.

The structure[8] and the numbering of the positions in *trans*-stilbene are shown in Fig. 1.

Results and Discussion

The spin distribution calculated with the semiempirical unrestricted SCF method and the observed coupling constants[1] and the spin densities[9] are tabulated in Table I.

Chang and Johnson[1] assigned coupling constants of 2.96 gauss and 1.90 gauss, which correspond to the spin densities of 0.132 and 0.0844 respectively,[9] to the *ortho*-protons, but they did not make clear which of these coupling constants is due to the proton in the C–H bond at the carbon atom 1 (1-proton) and which to that at the carbon atom 5 (5-proton). We obtained $\rho_1 = +0.1230$ and $\rho_5 = +0.1168$ as the spin densities at the *ortho*-carbons by means of our SCF calculation. Through a comparison of these coupling constants and calculated spin densities, we could assign the coupling constant of 2.96 gauss to the 1-proton and that of 1.90 gauss to the 5-proton. By then comparing the coupling constants of the *meta*-protons and the calculated spin densities at the *meta*-carbons, we could assign the coupling constant of 0.81 gauss to the 2-proton and that of 0.30 gauss to the 4-proton. The values in the second and in the third columns in Table I are written according to the above-mentioned assignment. The agreement between the observed spin distribution and the spin distribution calculated by means of the SCF method seems fairly good.

Spin distributions calculated by means of the HMO method and by means of the McLachlan procedure with $\lambda = 1.00$ are also listed in Table I for the sake of comparison.

The SCF and HMO calculations were carried out on the KDC-I digital computer of Kyoto University.

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[7] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[8] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.*, **A162**, 568 (1937).

[9] To calculate the spin density from the coupling constant, we used the following equation; $a_{\mu\text{-H}} = 22.5\,\lvert\rho_{\mu}\rvert$. H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).