

SHORT COMMUNICATIONS

SPIN DENSITY IN THE BENZYL RADICAL AS A FUNCTION OF THE METHYLENE ORIENTATION*

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In a recent paper¹ by the authors, a simple method of calculating positive and negative spin densities was outlined and applied to a number of systems. One of the systems chosen was the benzyl radical with the π -bonding p -orbital of the methylene group perpendicular to the plane of the ring (i.e. with a dihedral angle of 0°). The positive and negative spin densities found for this configuration were in excellent agreement with experimentally determined values. In view of the apparent importance² of the benzyl fragment in larger radical species such as phenyl-substituted aromatics, where steric hindrance could produce non-zero values for this dihedral angle γ , then the values of the spin densities in benzyl, determined as a function of γ , also become of interest.

Using the formalism of ref. 1, the variation with dihedral angle can be followed if the repulsion integrals $J_{12} = (\chi_1\chi_1|\chi_2\chi_2)$ are approximated by the charged sphere model of Parr.³ For the general case of p -orbitals at centres i and j , separated by a distance r , and oriented at a dihedral angle ν , the formula is:

$$J_{12}(\gamma, r) = (14 \cdot 395/2r)[\{1 + 2(R/2r)^2(1 - \cos \gamma)\}^{-1} + \{1 + 2(R/2r)^2(1 + \cos \gamma)\}^{-1}]$$

where R is the diameter of the charged sphere of each lobe. For any particular separation r , the variation of $J_{12}(\gamma, r)$ may be written as $J_{12}(\gamma, r) = J_{12}(0^\circ, r)G(\gamma, r)$. One finds when $R/2r \leq 1/3$, then $G(\gamma, r)$ becomes insensitive to the value of γ . For $R = 1.46 \text{ \AA}$ this means that $J_{12}(\gamma, r)$ is essentially independent of angle when r is greater than about 2.2 \AA .

It is well known that the charged sphere model does not give the proper values for J_{ij} when $r \leq 2.8 \text{ \AA}$, and semiempirical extrapolation methods have been developed⁴ for these small separations. However, we assume that the dependence on angle is still given by $G(\gamma, r)$, and can then write $J_{12}(\gamma, r)$ as the product of the value of $J_{12}(0^\circ, r)$, as obtained by the semiempirical extrapolation method, times the function $G(\gamma, r)$. The dependence on angle of the one-electron core integrals is given simply as

$$H_{\text{core}, ij}(\gamma, r) = \cos \nu \{H_{\text{core}, ij}(0^\circ, r)\}$$

if $(2p_{iz}|H_{\text{core}}|2p_{iy})$ is taken to be zero.

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¹ Adam, F. C., and Laidlaw, W. G., *Aust. J. Chem.*, 1966, **19**, 897.

² Falle, H. R., and Adam, F. C., *Can. J. Chem.*, 1966, **44**, 1387; Adam, F. C., and Falle, H. R., *Can. J. Chem.*, 1966, **44**, 1397.

³ Parr, R. G., *J. chem. Phys.*, 1952, **20**, 1499.

⁴ Pariser, R., and Parr, R. G., *J. chem. Phys.*, 1953, **21**, 767.

The results obtained using the split shell method¹ for the benzyl radical are plotted in Figure 1. The bridgehead, *ortho*, and *para* spin densities do not change sign over the range of values of γ . On the other hand, the *meta* spin densities do; as γ goes from 0 to $\pi/2$ the *meta* spin density changes from negative to positive. It is interesting to note that when $\gamma = 90^\circ$, which corresponds to complete lack of conjugation between the ring and the methylene group in a simple Hückel scheme, there is still considerable uncoupling of the spins within the ring system.

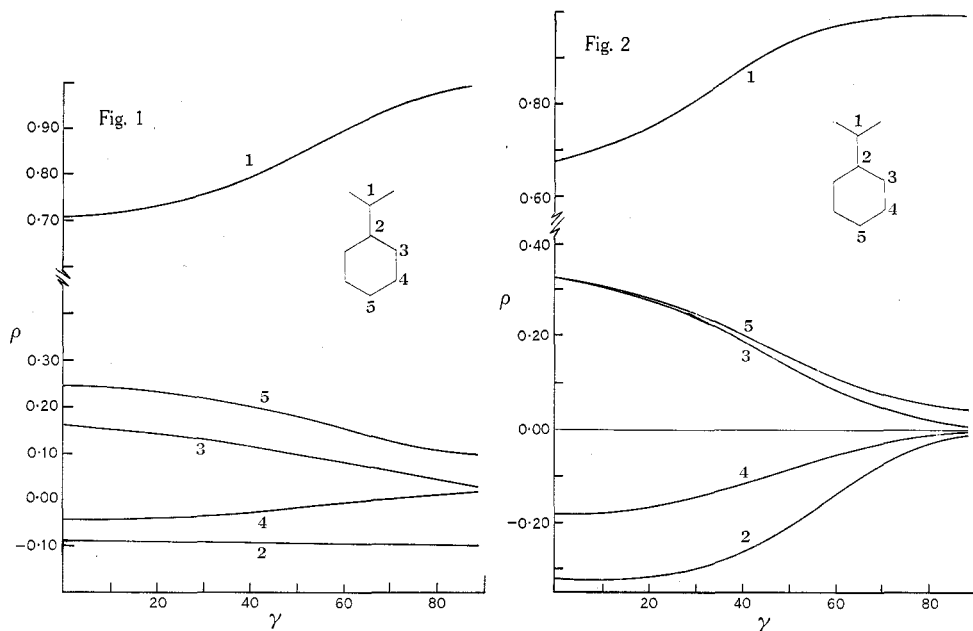


Fig. 1.—Spin densities in the benzyl radical as a function of dihedral angle (γ) computed by the "split shell" method.

Fig. 2.—Same, computed by the VB method.

The spin density distribution as a function of ν may also be obtained from a valence bond calculation if the exchange integral is taken to be

$$\alpha_{ij}(\gamma, r) = (\cos^2 \gamma) \alpha_{ij}(0^\circ, r)$$

Figure 2 depicts the results for such a valence bond treatment of the benzyl fragment when only nearest neighbour interactions are included. The results are similar in character to those of the "split shell" method, but the magnitude of the calculated spin densities are in general greater.

These results may be directly applied to radical derivatives of benzyl, where chemical substituents appear in either of the *ortho* positions of the ring, or on the extra cyclic carbon atom, or both, so as to produce a non-planar species. The conclusions may also be extended to a variety of compounds of which the ion-paired reduction products of benzaldehyde or of acetophenone might be cited. It is not immediately apparent but the calculations may also be applied to diphenylmethyl radical derivatives.

Falle and Adam² proposed that certain of their substituted diphenylmethyl radicals were undergoing a concerted rotation which may be described in terms of two dihedral angles γ_1 and γ_2 . These angles represent the angles between the p -orbital of the central carbon atom and the p -orbitals of the bridgehead carbon atoms in each of the two rings. During rotation these angles change from initial values of say, γ_1, γ_2 through all possible displacements from 0° to 360° , and back to γ_1, γ_2 . The observed spin densities would then be averaged values which would depend on the spin density distribution in each rotational configuration and upon the time spent in each configuration.

For molecules in which there is very considerable steric repulsion between the rings, the molecule will tend to assume configurations in which both γ_1 and γ_2 are 90° . If the diphenylmethyl species are then considered as the sum of the two benzyl radicals each with $\gamma = 90^\circ$ the spin densities are, from the MO treatment, $\rho_o = 0.02$, $\rho_m = 0.03$, $\rho_p = 0.10$; while from the VB treatment they are $\rho_o \approx 0$, $\rho_m \approx 0$, $\rho_p = 0.05$.

For diphenylmethyl derivatives in which there is still considerable steric repulsion between the rings, but less than the above extreme case, γ_1 and γ_2 would tend to be out of phase. If, for example, the molecule is spending most of the time in a configuration where $\gamma_1 = 0^\circ$ and $\gamma_2 = 90^\circ$ or $\gamma_1 = 90^\circ$ and $\gamma_2 = 0^\circ$ then the diphenylmethyl system may be treated as the averaged sum of a benzyl system with $\gamma = 0^\circ$ and a benzyl system with $\gamma = 90^\circ$. This represents a compromise between a partial loss of delocalization energy (as one ring is conjugated to the methylene and the other ring is not) and a partial reduction in the forces of steric repulsion. The average spin densities between these extremes may be obtained from Figures 1 and 2. For the MO treatment, $\rho_o = 0.09$, $\rho_m = -0.03$, $\rho_p = 0.17$, while for the VB treatment the values are $\rho_o = 0.17$, $\rho_m = -0.08$, $\rho_p = 0.20$, respectively. On the other hand, if the molecules reside principally in a configuration in which initially $\gamma_1 = 30^\circ$, $\gamma_2 = 60^\circ$ and then rotate to $\gamma_1 = 60^\circ$, $\gamma_2 = 30^\circ$, then the treatment of the diphenylmethyl system as a sum of perturbed benzyl systems is less obvious but the spin densities are approximately the same. In fact, as long as γ_1 and γ_2 are 90° out of phase (i.e. the hindered species) the spin densities will approximate those given above. Thus the spin densities of the symmetric rotomer with $\gamma_1 = \gamma_2 = 45^\circ$ are predicted to be nearly the same as those of the rotationally averaged unsymmetric conformers considered above.

For molecules experiencing very little steric repulsion γ_1 and γ_2 will both be closer to zero, and, as both Figures 1 and 2 indicate, there will be an increase in spin density at the ring positions. However, in cases such as this, the treatment of diphenylmethyl as the sum of two benzyl fragments may well be a rather more serious approximation.

The experimental values² for diarylmethyl systems cover the ranges

$$0.06 < |\rho_o| < 0.12, 0.04 < |\rho_m| < 0.06$$

and

$$0.14 < |\rho_p| < 0.16.$$

The upper limit of each range occurs with the least hindered species, as would be predicted from the foregoing treatment.