Evaporation of the benzene solution afforded 257 mg (72%) of trityl chloride, mp 108–111°. The identity was confirmed by mixture melting point and ir spectrum.

**Registry No.**—*N*-Hydroxyphthalimide, 524-38-9; *N*-trityloxyphthalimide, 31938-10-0; trityloxyamine, 31938-11-1; *O*-tritylacetoxime, 31938-12-2; *O*-tritylbenzaldoxime, 31938-13-3.

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## Electron Spin Resonance Investigation of the 2-Furanylmethyl Radical. Calculation of Its Geometry and Rotational Barrier by INDO

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Because of its great importance in the theory of odd alternant radicals, the benzyl radical has been repeatedly investigated both experimentally and theoretically.[1–4] Heterocyclic analogs of benzylic and similar radical systems have been largely unstudied. One exception is Hudson's[5] report of the esr spectra of both the 2-thenyl and 3-thenyl radicals generated in solution during the steady-state photolysis of di-*tert*-butyl peroxide in the presence of 2-methyl- and 3-methylthiophene, respectively. In both the 2-thenyl and 3-thenyl radicals, the methylene protons were nonequivalent, but $\pi$-electron calculations of the McLachlan approximate SCF method did not provide any insight into this nonequivalence.[5] As long as the methylene group's rotational barrier is large, one would expect nonequivalence from a consideration of symmetry. Similar examples of magnetic inequivalence include the allyl[6] and substituted allyl[7] radicals. In these radicals more sophisticated, all-valence electron calculations, such as the INDO technique, correctly predict this inequivalence.[8]

We now report the esr spectrum of the 2-furanylmethyl radical, I, which was obtained during the steady-state photolysis of solutions of di-*tert*-butyl peroxide and 2-methylfuran at temperatures between $-30$ and $-80^\circ$ in the esr cavity.[9] The spectrum exhibited 32 lines due to the inequivalence of the methylene protons and showed a signal to noise ratio at $-80^\circ$ similar to that observed[5] for the 2-thenyl radical. The inequivalence persisted even at $-30^\circ$ and the only change in the spectrum observed on warming was a drastic decrease in intensity.

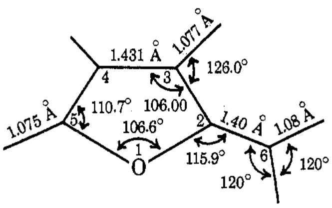


Figure 1.—Geometry of radical I used in INDO calculations.

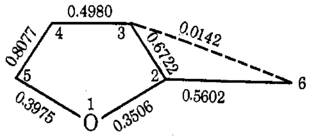
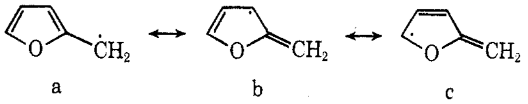


Figure 2.—Calculated $\pi$-bond orders of the 2-furanylmethyl radical.



I

The experimental hyperfine splittings, as determined by a computerized best fit to the experimental spectrum, are listed in Table I. Table II summarizes the $g$ values determined for the benzyl, 2-thenyl, and 2-furanylmethyl radicals.[10] The $g$-value variation is both a function of the size of the spin–orbit coupling for carbon, oxygen, and sulfur and the energy of the molecular orbital occupied by the odd electron.[11] The 0.0004-$g$ value increase for the 2-thenyl over the 2-furanylmethyl radical is a measure of the increase in the size of the spin–orbit coupling constant for sulfur and the amount of sulfur d- and p-orbital contribution to the radical. However, the difficulty of measuring the radical's excitation energy and the number of its excited states contributing to the $\Delta g$ shift prevents a determination of the sulfur d-orbital contribution. Nevertheless, the larger isotropic $g$ value of 2.0061 observed for the thiophene-2-carboxylic acid radical[12] suggests only a small sulfur d- and p-orbital contribution in the thenyl radical.

A series of INDO[8] calculations[13] were performed on I using the bond angles and lengths for the furan portion obtained by Bak[14] in his microwave study of furan. The methylene group was then attached and the parameters used are summarized in Figure 1.[15] The calcu-

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(1) A. Carrington and I. C. P. Smith, *Mol. Phys.*, **9**, 137 (1965).

(2) A. Carrington, *Quart. Rev., Chem. Soc.*, **17**, 67 (1963).

(3) A. Carrington, J. R. Bolton, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

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(6) R. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(7) R. Livingston and H. Zeldes, *ibid.*, **44**, 1245 (1966).

(8) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(9) The uv light from a 500-W PEK 500-2 lamp was filtered by a water filter and was focused on a sample held in a quartz variable-temperature esr dewar by a quartz condenser lens added to the quartz optics of a standard PEK M910 housing. Similar techniques to those previously reported by Kochi and Krusic were used. See J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 1877, 1879, 3938, 3940, 3942, 3944, 6161 (1969); **93**, 846 (1971).

(10) The benzyl and 2-thenyl radicals were prepared in this study by the same photolysis technique used to generate the 2-furanylmethyl radical.

(11) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); **7**, 311 (1964). B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(12) B. Eda, R. J. Cook, and D. H. Whiffen, *Trans. Faraday Soc.*, **60**, 1497 (1964).

(13) The INDO program (cnindo, QCPE No. 141) was obtained from the Quantum Chemistry Program Exchange, Indiana University, and it was modified for use on a Univac 1108 computer.

(14) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Hygaard, J. R. Anderson, and M. Schottlander, *J. Mol. Spectrosc.*, **9**, 124 (1962).

(15) The only bond which was optimized in the calculations was the 2–6 bond. While the bond distances in the ring will certainly change upon interaction with a $CH_2\cdot$ side chain, these changes would be relatively small.

TABLE I

THEORETICAL AND EXPERIMENTAL HYPERFINE SPLITTING CONSTANTS (IN GAUSS), CALCULATED CHARGE DENSITIES, AND S-ORBITAL SPIN DENSITIES FOR 2-FURANYLMETHYL RADICAL

| | | Position of hydrogen | | | | |
|---|---|---|---|---|---|---|
| | | 3 | 4 | 5 | 6 | 6 |
| Experimental hfs | | 8.79 ± 0.03 | 1.28 ± 0.02 | 7.87 ± 0.03 | 13.32 ± 0.03 | 13.01 ± 0.03 |
| Calculated (INDO) | *a* | 9.40 | 3.29 | 6.44 | 14.79 | 14.67 |
| | *b* | 8.23 | 2.93 | 5.59 | 16.59 | 16.49 |

| | Atom | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| s-Orbital spin density | 0.0011 | −0.0180 | 0.0217 | −0.0120 | 0.0153 | 0.0340 |
| Charge density[c] | −217.0 | +217.9 | −43.9 | −29.4 | +164.9 | −97.6 |

[a] Calculated using the 2–6 bond distance of 1.40 Å; this was the minimum energy calculation. [b] Calculated using the 2–6 bond distance of 1.46 Å. [c] Charge densities × $10^3$.

TABLE II

THE *g* VALUES FOR BENZYL, 2-THENYL, AND 2-FURANYLMETHYL RADICALS IN SOLUTION

| Radical | Average value of *g*, G[a] |
|---|---|
| Benzyl | 2.00252 |
| 2-Furanylmethyl | 2.00269 |
| 2-Thenyl | 2.00312 |

[a] These values are the average of six individual determinations, with an approximate error of ±0.0001 G.

lated values of the hyperfine splittings summarized in Table I compare very closely with the observed spectrum and emphasize the inequivalence of the methylene protons. Table I also lists the s-orbital spin densities and atomic charge densities in I. The charge densities illustrate oxygen's high electronegativity, and adjacent carbons, 2 and 5, bear significant positive charge. As predicted by valence-bond theory, the largest amount of spin density is concentrated on carbons 6, 3, and 5. This is in agreement with the short 2–6 bond length of 1.40 Å, which indicates the existence of significant 2–6 double bond character and suggests that a large rotational barrier should exist. The calculated π-bond orders (shown in Figure 2) further substantiate this view. The 2–3 and 4–5 bonds have the highest π-bond order (see Ia), but the large π-bond order of the 2–6 bond indicates that resonance hybrids Ib and Ic may be correctly invoked in portraying a valence bond structure. Furthermore, the moderately high π-bond order of the 3–4 bond supports the use of Ic.

The barrier to rotation about the 2–6 bond was calculated. The planar conformation was found to be 25.16 kcal/mol more stable than the conformation in which the plane of the methylene group is perpendicular to the plane of the ring.[16] This large rotational barrier explains the observed spectral inequivalence of the methylene protons at −30° and further demonstrates the strong electronic interaction of the methylene group with the ring.

In conclusion, the inequivalence of the methylene protons in the 2-furanylmethyl radical has been explained, and good agreement with the esr hyperfine splittings has been obtained using an INDO molecular orbital calculation based on the experimental microwave structural data of furan providing that the 2–6 bond (methylene) distance has been optimized.

**Registry No.**—2-Furanylmethyl, 31902-01-9; benzyl, 2154-56-5; 2-thenyl, 25879-26-9.

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[16] As expected, the methylene protons become equivalent in this perpendicular conformation.

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## Polar Tautomer Dimerization of Ionic Arylazonaphthols in Water

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Recent spectroscopic investigations[1] on the aggregation of ionic 1-phenylazo-2-naphthols in aqueous and methanolic solutions have shown the existence of monomer–dimer equilibria in the $10^{-6}$–$10^{-4}$ *M* concentration range. The absorption spectra of the ionic hydroxy azo dyes with increasing dye concentration clearly indicate a decrease in the absorptive strength of the main absorption band accompanied by a hypsochromic shift in the peak maxima. The dimer spectra for several ionic 1-arylazo-2-naphthols show a strong H band on the high energy side of the monomer band and a weaker J band on the low energy side of the monomer transition. A study of the aggregation of this class of compounds is complicated by the fact that the molecules can exist in a quinone–hydrazone ⇌ azo–enol tautomeric equilibrium.

In this note we report on the dimerization processes involving the tautomeric species involved in eq 1. The BR-2 compound is a common ionic arylazonaphthol compound known as Bonadur Red. It has recently been spectroscopically shown to exist as a quinone–

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