on rate has actually been recognized. In fact, Hammett-type correlations are now so generally expected in reactions which involve free radicals that Jaffé's review of these reactions[3] tabulated correlations of rate ratios with σ without mentioning that the dimerization of triarylmethyl radicals cannot be correlated in this manner. Evidently the proposal by Walling, Mayo, and coworkers[34] that transition states in radical reactions are stabilized substantially by polar effects which involve electron pair delocalization applies quite generally,[51,52] and the rates are correlated better by σ^+ than by σ.[53] The structures of the transition states in these reactions are such that delocalization of an unshared electron pair becomes possible (although it would not be possible in the isolated radicals), and this determines substitution behavior in the same manner as in the hydrazyls. It may turn out that only dimerization reactions, in which polar effects cannot be large, will display class S effects of substitution on rates or equilibria.

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(51) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

(52) P. D. Bartlett and G. Rüchardt, *ibid.*, **82**, 1760 (1960).

(53) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

Substituent Effects on the Properties of Stable Aromatic Free Radicals. An LCAO–MO Treatment[1]

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Abstract: Simple LCAO–MO calculations have been carried out for the 1-picryl-2,2-diphenylhydrazyl and triphenylmethyl free radicals, and for their derivatives which contain two or three nitro or methoxy groups. Details of the unpaired electron distribution in the hydrazyl radicals are more closely reproduced when the parameters used are evaluated systematically. The coulomb integrals are determined from orbital electronegativities for atoms in the correct valence states, corrected for the number of electrons contributed to the π system and for formal charge. Exchange integrals are determined from bond lengths, with the assumption that a bond with a given overlap integral has the same exchange integral as a carbon–carbon bond with the same overlap. The calculations also include a study of the effect of rotation of an aromatic ring on its interaction with two orthogonal 2p atomic orbitals on an adjacent atom which is assumed to be sp hybridized. The results of these calculations reproduce the trends in optical spectra and unpaired electron densities (these must be assumed to be systematically related to the observed nitrogen hyperfine coupling constants) which led to the empirical division of free radicals into two classes, based upon effects of substitution on these properties. The parameters which give the optimum fit of properties of the three hydrazyl radicals are used to predict effects of other types of substitution in this free-radical system. The results show that MO calculations with input parameters whose values lie in a reasonable range can give a wide range of unpaired electron densities on the hydrazine nitrogen atoms, and thus cannot be used to establish the relative values of these densities.

This paper presents the results of a theoretical study of the effects of substitution on the optical and esr spectra of two types of stable aromatic free radicals. Experimentally, substitution effects in the 1-picryl-2,2-diarylhydrazyl and the triarylaminium salt free radicals have been shown to fall into two different patterns.[2] In the former, electron-donor and electron-acceptor substituents in the *para* positions of the two aromatic rings shift both the nitrogen esr hyperfine coupling constants and the positions of the longest wavelength absorption bands in opposite directions. Free radicals which display this behavior have been labeled class O. In the triarylaminium salts, both types of substituents shift each of these properties in the same direction. Free radicals of this type have been labeled class S. A structural criterion has been proposed for the assignment of other types of aromatic free radicals to the two classes represented by these two series of compounds,[2] and the triarylmethyl radicals fit the assignment to class S on the basis both of their structures and somewhat meager data on their experimental behavior. The additional complications which arise in treating the ionic charge on the aminium salts led to the choice of the triarylmethyl free radicals as representatives of class S in carrying out these computations.

No systematic theoretical treatment of substitution effects in these free radicals has been carried out, although calculations have been reported on the unsubstituted compounds. The results of both simple MO and VB computations for triphenylmethyl have been summarized by Karplus and Fraenkel.[3] Comparison with the experimental data shows that there is not a great deal to choose between the quantitative results of the two methods, except in the respect that the VB

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(1) Most of this work was carried out at Columbia University and the University of Minnesota while the author held a National Science Foundation Science Faculty Fellowship in 1960–1961. It is a pleasure to acknowledge the help of Professor Martin Karplus, whose constant interest and generous contributions of advice and background information made it possible to carry out this study. The author is also indebted to the IBM Watson Scientific Laboratory, the Control Data Corporation, and the NASA Institute for Space Studies for donations of computer time.

(2) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

(3) (a) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); (b) see Table VII of ref 3a.

method predicts the observed negative spin densities at the *meta* carbon atoms of the aromatic rings, while the simple Hückel method predicts that the densities at these atoms will vanish. A very rough VB computation for DPPH has been reported by Brown, Anderson, and Gutowsky.[4] This also predicts negative spin densities at the positions *meta* to the two hydrazine nitrogen atoms, and this prediction was confirmed by observation of the proton nmr shifts in polycrystalline samples of the radical at 77°K. These data require that equal numbers of ring protons be exposed to unpaired electron spin in each of the two possible directions. Stated another way, they require that positive unpaired electron spin be associated with the same number of *ortho* plus *para* carbon atoms as the number of *meta* carbon atoms at which the electron spin is in the negative direction. This can be true only if the unpaired electron is delocalized over the picryl as well as the two phenyl rings in this radical. A simple LCAO–MO calculation for DPPH has been reported by Bersohn.[5] The results of this computation have been said to establish the relative magnitudes of the spin densities on the two hydrazine nitrogen atoms.[6] This is incorrect, as the results presented here show.

The computational results of greatest interest to us are the energy differences between the two upper occupied and the lowest empty MO, which are related to the optical spectra, the unpaired electron densities on the two hydrazine nitrogen atoms of the hydrazyls, and the densities on the methyl carbon atoms of the triarylmethyl radicals. All of these densities should be large and positive. For this reason, the failure of simple MO calculations to predict negative spin densities is not of much importance for our present purposes, since small negative spin densities on some of the ring carbon atoms are compensated by small increases in the positive densities on the hydrazyl nitrogens or the methyl carbon. The MO method has the advantage that it is more straightforward to apply to systems which contain many heteroatoms, so it was selected for these computations.

Computations

Figure 1 shows the numbering scheme used in these computations to identify the various atoms which participate in the π systems of these radicals.

Molecular Geometry. The triarylmethyl radicals are assumed to have coplanar bonds from the methyl carbon to each of the three aromatic rings, although this has not been experimentally demonstrated. These three bonds certainly are twisted to reduce overlap of the hydrogen atoms in the *ortho* positions on the rings. This twist angle has been estimated to be 32° by Adrian,[7] and is allowed for in the computations by multiplying the C_0–C_1 exchange integrals by the factor cos θ. The measured (crystallographic) values in some triarylcarbonium perchlorates are in the range 30–35°.[8]

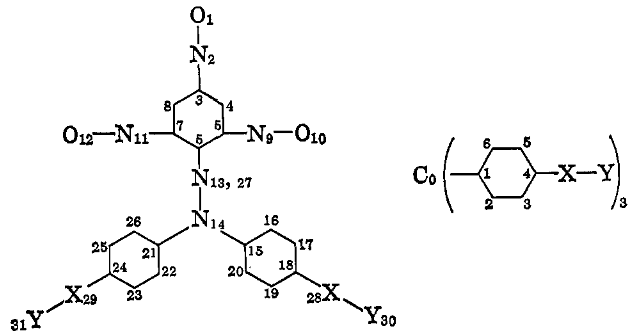
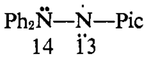


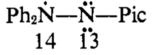
Figure 1. In the unsubstituted compounds, X and Y are absent. In the nitro-substituted compounds, X is N, and Y is O. In the methoxy-substituted compounds, X is O and Y is absent.

The geometry of the hydrazyl system is more complicated. The unpaired electron must be delocalized to both nitrogen atoms 13 and 14, on the basis of the N^{14} nuclear hyperfine splitting observed in the esr spectrum. It is required to be delocalized through the aromatic rings and also through the picryl ring on the basis of the nmr data of Brown, Anderson, and Gutowsky.[4] The three bonds to nitrogen number 14 are assumed to be coplanar, and the attached benzene rings to be twisted 30–35° about these bonds, by analogy with the triphenylmethyl case. This geometry provides a continuous π system from the two rings (corrected for the twist angle) through the p_z atomic orbitals on nitrogen atoms 14 and 13. The π system on the picryl ring must overlap the 2p AO which contains the unpaired electron on nitrogen 13, in order to permit delocalization of the unpaired electron into this ring. The picryl ring must meet a second requirement, however. Delocalization of the unpaired electron from nitrogen 13, in formula I, to nitrogen 14 in formula II, produces an unstable accumulation of charge on 13. This can be stabilized by transfer of an electron pair to the picryl group, as in III. A significant contribution of this structure to the resonance hybrid is indicated by the large increment in dipole moment of the hydrazyl radical relative to the 1-picryl-2,2-diphenylhydrazine.[9] There is no experimental information on which of the two unshared pairs in II is donated to the picryl ring. For these calculations, atom 13 has been assumed to be sp hybridized. Its p_z AO is then capable of overlap with the π system of the picryl ring. The angle between the plane of the three bonds to atom 14 and the plane of the picryl ring (with the picryl ring rotated about the 6–13 bond axis) defines the twist angle φ. As φ increases, interaction between orbital 13 which contains the unpaired electron, and the picryl ring, decreases in proportion to cos φ. Similarly, the interaction between the unshared electron pair in the p_y AO (assigned number 27) and the picryl ring increases in proportion to sin φ. Examination of models shows that some rotation of either the picryl ring or of the two *ortho* nitro groups on it is necessary because of overlap with the σ-hydrogen atoms of the



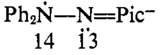
$\underset{14}{\mathrm{Ph_2}\overset{\cdot\cdot}{\mathrm{N}}}-\underset{\underset{13}{\cdot\cdot}}{\overset{\cdot}{\mathrm{N}}}-\mathrm{Pic}$

I



$\underset{14}{\mathrm{Ph_2}\overset{+}{\dot{\mathrm{N}}}}-\underset{\underset{13}{\cdot\cdot}}{\overset{-}{\ddot{\mathrm{N}}}}-\mathrm{Pic}$

II



$\underset{14}{\mathrm{Ph_2}\overset{+}{\dot{\mathrm{N}}}}-\underset{\underset{13}{\cdot\cdot}}{\mathrm{N}}{=}\mathrm{Pic}^-$

III

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(4) T. H. Brown, D. H. Anderson, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 720 (1960).

(5) (a) R. Bersohn, *Arch. Sci.* (Geneva), 11, 172 (1958). There was an error in Bersohn's matrix, so the spin densities reported in this reference are incorrect. See the recomputed values in Table II of the text. (b) Parameters were estimated by Bersohn according to the method suggested by Coulson: C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, pp 242, 243.

(6) N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, **34**, 1708 (1961).

(7) F. J. Adrian, *ibid.*, **28**, 608 (1958).

(8) Private communication from Professor Klaas Eriks.

(9) J. Turkevich, P. F. Oesper, and C. P. Smythe, *J. Am. Chem. Soc.*, **64**, 1179 (1942).

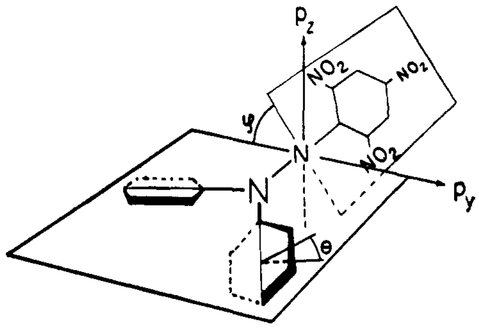

Figure 2. Perspective drawing of the 1-picryl-2,2-diphenylhydrazyl free radical. The assumed geometry around the hydrazine nitrogen atoms is shown, together with the angles φ and θ, and the directions of the p_z and p_y atomic orbitals on the picryl nitrogen.

phenyl rings. (The increased distance between the picryl ring and atom 14 which results from the insertion of atom 13 is approximately compensated by the greater size of the nitro groups, compared with covalently bonded hydrogen.) If only the picryl ring twists, the minimum angle is about 30°. Rotation of the *ortho* nitro groups relative to the plane defined by the picryl ring defines the angle τ. The geometry of this system is indicated in Figure 2. There is some evidence to justify the hybridization assumed for nitrogen 13, since the computations of Lord and Blinder[6] suggest cylindrical distribution of charge about this atom. Furthermore, if this atom should be sp^2 hybridized, the minimum value for φ exceeds 50°. This decreases overlap with the p_z AO on atom 13, and consequently reduces the unpaired electron density on the picryl ring.

Estimation of MO Parameters. The molecular orbital method requires a value for the coulomb integral for each heteroatom which contributes to the π system, and an exchange integral for each bond which involves any of these atoms. To minimize the number of necessary parameters, the methoxy group was selected as a typical donor group for use in both types of free radical, and the nitro group (which is already present in the picryl ring) as a typical acceptor. In handling these substituents, use is made of Wheland's convention[10] that all *ortho,para*-directing substituents can be treated as a single atom which possesses an unshared electron pair, and all *meta*-directing groups can be reduced to a two-atom system connected by a multiple bond. Thus, $-OCH_3$ is regarded as $-\ddot{O}$, and $-NO_2$, as $-N{=}O$. A variety of methods have been used to estimate coulomb and exchange integrals, and a wide range of values has been used by various atuhors.[11,12] The results of a few preliminary computations showed that these parameters cannot be assigned simply by adjusting them so that the computed results fit the experimental data on spectra and coupling constants. Consequently, methods were developed for systematically estimating both types of constants.

The usual scheme for estimating exchange integrals has been based upon Mulliken's demonstration that exchange integrals are roughly proportional to the overlap integrals for the same bonds.[13] The overlap integrals are available in tabular form.[14] A slightly different scheme is used here: a bond between atoms i and j with overlap integral S_{ij} is assumed to have the same exchange integral as the carbon–carbon bond whose overlap integral also equals S_{ij}. Exchange integrals for carbon–carbon bonds of various lengths are evaluated from the Longuet-Higgins and Salem[15] equation. Thus, for any bond between atoms i and j whose length can be estimated, the corresponding overlap integral is determined, then the length of the carbon–carbon bond with the same overlap integral, and finally the exchange integral which corresponds to this carbon–carbon length. The process can be carried out from a single graph on which S_{ij}, S_{cc}, and β_{cc} are all plotted against bond length. Additional rationalizations for this procedure and tests of it will be reported elsewhere. Bond lengths are based upon mean experimental values reported by Sutton,[16] corrected where necessary for changes in hybridization of the bonded atoms.[17] The bond length is assumed to decrease 0.04 A for each step change in hybridization of either of the two bonded atoms from sp^3 to sp^2 to sp.

Coulomb integrals were estimated from the orbital electronegativities computed by Hinze and Jaffé,[18] with appropriate corrections for the formal change on the atom and for the number of electrons donated by it to the π system. The relationship used is given in eq 1.

$$\alpha_i = \alpha_c + [(\chi_i - \chi_c)/3.4 + (n - 1) + z]\Delta\beta_{cc} \quad (1)$$

In this equation, χ_i is the orbital electronegativity of the 2p AO in the appropriate (sp or sp^2) configuration of the heteroatom i, and χ_c the electronegativity of the 2p AO of the sp^2 carbon atom. Their difference is divided by 3.4, the electronegativity difference estimated to correspond to transfer of unit charge, from Pauling's approximation[19] that an electronegativity difference of 1.7 corresponds to 50% ionic character in σ bonds. This is a very rough estimate for the effects transmitted through the π system with which we are concerned here, but no better figure is known to us. The parameter n is the number of electrons donated to the π system by atom i, and z is the formal charge on this atom. The correction in the Coulomb integral is expressed in terms of the carbon–carbon exchange integral, β_{cc}. The parameter Δ (which corresponds to Streitwieser's ω)[11] is the increment in α_c which corresponds to transfer of unit charge to the carbon atom. Δ was evaluated by requiring that it give eq 2 for the

$$\alpha_N = \alpha_C + 0.22\beta_{cc} \quad (2)$$

coulomb integral for the pyridine nitrogen. This is the "optimum" value obtained by McWeeny and Peacock.[20] The Δ so obtained equals 0.91. This is

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(10) G. W. Wheland, *J. Am. Chem. Soc.*, 64, 900 (1942).

(11) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961: (a) Chapters 4 and 5; (b) p 115; (c) p 135.

(12) An amusing series of values for α_N, each "supported" by its successful use to compute the dipole moment of pyridine, has been reported by A. T. Amos and G. G. Hall, *Mol. Phys.*, 4, 25 (1961).

(13) R. S. Mulliken, *J. Chim. Phys.*, 46, 497 (1949).

(14) R. S. Mulliken, C. A. Reicke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

(15) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), A251, 172 (1959).

(16) L. E. Sutton, Ed., Special Publication No. 11, The Chemical Society, London, 1958.

(17) H. A. Bent, *Chem. Rev.*, 61, 275 (1961).

(18) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 84, 545 (1962).

(19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 100.

(20) R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.* (London), A70, 41 (1957).

Table I. Parameters for LCAO-MO Calculations

	Increments in coulomb integrals, β			
Atom	Bersohn[a]	Streitwieser[b]	Systematic[c]	"Optimum"[c]
O in $-NO_2$	1.0	1.0	0.41	0.7
N in $-NO_2$	0.5	2.0	1.12	1.12
N_{13}	0.5	0.5	0.22	0.5
N_{14}	0.5	1.5	1.12	0.9
N_{27}	...	1.5	1.12	1.12
O in $-OCH_3$	1.0[e]	2.0	1.32	1.32

		Exchange integrals, β			
Bond	Assumed length, A	Bersohn[a]	Streitwieser[b]	Systematic[c]	"Optimum"[c]
N—O in $-NO_2$	1.21	$1.0\sqrt{2}$	$0.7\sqrt{2}$	$0.56\sqrt{2}$	$0.56\sqrt{2}$
C—N to $-NO_2$	1.49	1.0	0.8	0.45	$0.45 \cos \tau$
C_6—N_{13}	1.35	1.0	$0.8 \cos \varphi$	$0.74 \cos \varphi$	$0.74 \cos \varphi$
N_{13}—N_{14}	1.32[d]	1.0	0.8	0.55	0.55
C_6—N_{27}	1.35	...	$0.8 \sin \varphi$	$0.74 \sin \varphi$	$0.74 \sin \varphi$
C—N_{14}	1.39	1.0	0.8 cos 32°	0.64 cos 32°	0.64 cos 32°
C—O to $-OCH_3$	1.36	1.0[e]	0.8	0.45	0.45
C—C_6H_5	1.42[f]	1.0	1.0	0.93 cos 32°	0.93 cos 32°

[a] See ref 5. Parameters were evaluated by the procedure given by Coulson.[5b] [b] See ref 11c. [c] See text. [d] The bond length in hydrazine (1.42 A) is shortened 0.12 A for sp^2–sp hybridization of the two nitrogen atoms. [e] These parameters were added to the set used by Bersohn in order to carry out computations for the OCH_3 substituent. [f] Estimated C–C_6H_5 distance. The crystallographic value is 1.42 A in $(C_6H_5)_3C^+ClO_4^-$. See ref 8.

appreciably smaller than the values which are often used for ω, but has the advantage that iterative computations generally will converge. They will not do so (or at best converge very slowly) in most cases when ω exceeds unity. The parameters estimated in this manner do not appear too outlandish in comparison with the usual ranges of the conventional values. These systematic parameters, together with values suggested by other authors which were used in some of the trial calculations, are listed in Table I.

Evaluation of Results. It should first be emphasized that the computed unpaired π-electron density on atom i, ρ_i^π, is not an experimentally accessible quantity. The observed parameters are the nitrogen hyperfine coupling constants, a^{N_i}.[2] The relationship between these quantities has been investigated for C^{13} hyperfine splittings,[3] but it is not known for the N^{14} case. In fact, one would expect different relationships for the hydrazyl nitrogen atoms in positions 13 and 14 if they are in fact differently hybridized in the actual molecule, as assumed here.

It would be worthwhile to consider these difficulties in greater detail. The N^{14} hyperfine splitting observed in the simple radical $\cdot{}^+NH_3$ is 19.3 oersteds.[21] This is attributed to polarization of the shared electrons in the three N-H bonds by the unpaired electron in the $2p_z$ AO of the nitrogen atom. This polarization results in a small excess probability that the three bonding electrons whose spin is parallel to that of the electron in the p_z AO will be at the N^{14} nucleus. The electron–nuclear interaction which results produces the hyperfine splitting. In $\cdot{}^+NH_3$ and all of the nitrogen radicals, there is an additional contribution to the splitting from polarization of the 1s electrons. However, this case is simpler than the delocalized π-electron radicals with which we are concerned: in these molecules, there are additional contributions to the hyperfine splitting by a given nucleus which result from polarization of the bonding electrons by the unpaired spin density in the $2p_z$ AO at each of the atoms to which the nitrogen is bonded.[3,22] These will be small contributions to the N^{14} splittings for the triarylaminium ion radicals (and to the C^{13} splitting for the methyl-labeled triarylmethyl radicals) because the (negative) spin density in the $2p_z$ AO of the C_1 ring carbons to which the central nitrogen atom is bonded is small relative to that on the nitrogen. Furthermore, one would expect that the variation with substitution in density at the C_1 atoms would be relatively small. The result is that the observed C^{13} or N^{14} coupling constants should be very nearly proportional to the spin densities at these atoms. The computed spin densities on the methyl carbon atoms of the substituted triarylmethyl radicals are compared with the experimentally accessible N^{14} hyperfine coupling constants for the corresponding aminium salt free radicals.

This proportionality probably does not hold for the N^{14} splittings in the hydrazyl radicals, where the spin density is also high on the adjacent nitrogen, and varies in the opposite direction. An attempt to adjust the parameters computed by Karplus and Fraenkel for C^{13} hyperfine splittings to fit the N^{14} case has not been successful; too many assumptions are required to adjust the C^{13} interactions to those appropriate for N^{14}, and to satisfy geometric requirements assumed for the hydrazyls. Neither has an attempt to use the empirical parameters derived from the esr spectra of polyazine negative ions by Stone and Maki.[23] The uncertainties are so great that one cannot be certain that the larger coupling constant associated with nitrogen 13 really means that the unpaired electron density in the $2p_z$ orbital at atom 13 is greater than that at 14. This does seem likely, and it will hereafter be assumed to be the case. In addition, the lack of a relationship between spin densities and coupling constants means that one does not know the extent to which the unpaired electron is concentrated on the hydrazine nitrogen atoms. We arbitrarily look for spin densities of the order of 0.4 and 0.3 on nitrogen atoms 13 and 14, in view of the

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(21) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

(22) F. C. Adam and S. I. Weisman, *J. Am. Chem. Soc.*, **80**, 2057 (1958).

(23) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).

Table II. Computed Unpaired Electron Densities on the Central Atoms of Two Types of Free Radicals

Radical	Atom	Exptl a^{N_i}, oersteds	Computed ρ_i^{π} using parameters listed: Bersohn[a]	Streitwieser[a]	Systematic[a]	"Optimum"[b]
Dinitrohydrazyl	13	10.78[c]	0.136	0.122	0.425	0.202
	14	6.66	0.159	0.036	0.098	0.124
	13/14	1.62	0.855	3.39	4.33	1.63
Unsubstituted hydrazyl	13	9.90	0.114	0.034	0.432	0.191
	14	7.63	0.206	0.031	0.109	0.147
	13/14	1.30	0.553	1.09	3.97	1.30
Dimethoxyhydrazyl	13	9.25	0.064	0.014	0.422	0.178
	14	7.72	0.205	0.019	0.111	0.147
	13/14	1.20	0.312	0.74	3.80	1.21
Tris(*p*-nitrophenyl)methyl	C_0	. . .	0.252	0.057	0.282	0.129
Triphenylmethyl	C_0	0.674[d]	0.308	0.308	0.416	0.416
Tri-*p*-anisylmethyl	C_0	. . .	0.268	0.297	0.407	0.407

[a] Assumed angles are $\varphi = 45°$, $\tau = 0°$. [b] Assumed angles are $\varphi = 0°$, $\tau = 27°$. [c] Coupling constants for the hydrazyls are from M. M. Chen, C. V. Sane, R. I. Walter, and J. A. Weil, *J. Chem. Phys.*, **65**, 713 (1961). [d] From ref 22.

large total hyperfine splitting (17.5 oersteds) by these two nuclei.

The hydrazyl computations appear to be more sensitive than those for the triarylmethyl systems to the values used for the input parameters. Consequently, the various sets of parameters used were evaluated by testing the results for the hydrazyls against the experimental behavior of these systems. Two criteria were used to evaluate the parameters selected in terms of the results of the calculations. In the first place, they should reproduce all of the observed directions (but not the magnitudes) of change in $a^{N_{13}}$, $a^{N_{14}}$, and $a^{N_{13}}/a^{N_{14}}$, when the *para* substituents OCH_3 or NO_2 are introduced into the two aromatic rings of the hydrazyl radical. Use of this criterion minimizes the difficulty due to lack of relationships between ρ_{N_i} and a^{N_i}. Whatever the factors which relate these quantities for the nitrogen atoms in positions 13 and 14, they will not change greatly when substituents are introduced. Consequently, predictions of directions of change should be much more reliable than predictions of magnitudes. The second criterion was that the calculated energy states correspond qualitatively to the observed changes in the longest wavelength optical absorption peaks of these radicals. Since the MO method usually gives rather poor predictions of spectra, only shifts in the appropriate direction for the spectra of the substituted compounds were expected. After the computations were evaluated by their ability to fit the experimental properties of the hydrazyls, the same parameters were then used in computations for the triarylmethyl radicals also.

The computed spin densities failed to reproduce all of the observed changes in coupling constants when the systematically evaluated parameters were used. Certain of these parameters were then altered empirically to optimize the results for the three test compounds, and additional computations were then carried out to predict the effects of other types of substitution in these molecules. In all cases, parameters determined for the hydrazyl computations were also used for the triarylmethyl systems.

All computations were carried out with neglect of overlap, using a computer program for matrix diagonalization by the method of Jacobi. They were carried through one cycle only; no effort was made to iterate to self-consistency. The results of these computations are summarized in Table II. The spin densities in each column there were determined with the parameters listed in corresponding columns of Table I.

Discussion

All computations give changes in the ratios of unpaired electron densities on the hydrazine nitrogens, ρ_{13}/ρ_{14}, which parallel those in the observed coupling constants ratios, a^{13}/a^{14}. Introduction of nitro groups raises this ratio, and introduction of methoxy groups lowers it in calculations with any reasonable input parameters. Usually the changes in individual spin densities do not parallel the individual coupling constants as well. In particular, it is difficult to reproduce both the increase observed in a^{13} in the dinitro-substituted compound, and the small increase in a^{14} in the dimethoxyhydrazyl. In addition, all computations predict shifts in the optical absorption bands of the hydrazyls which are in the directions observed for the substituted radicals. When the same parameters are applied to computations for the triarylmethyl systems, reduction in the unpaired electron density at the methyl carbon and red shifts in the optical absorption bands are predicted for both of the substituted radicals. However, the magnitudes of these changes sometimes are disproportionate for the two different substituents. Thus the MO calculations reproduce the general features of optical and esr spectra which led to the division of free radicals into two classes on the basis of the changes in these properties on substitution.[2]

Computations carried out with Bersohn's parameters (evaluated according to the procedure described by Coulson[6b]) are not satisfactory for a number of reasons: the spin densities on both hydrazine nitrogen atoms are too low, ρ_{13} is less than ρ_{14}, and ρ_{14} decreases when methoxy groups are introduced. Streitwieser's suggested parameters,[11c] which were not corrected for deviations from "average" bond lengths, are still less successful. The computed spin densities on the nitrogen atoms are far too low, and the directions in which ρ_{13} changes on substitution are wrong. The results are even worse if the Streitwieser exchange integrals are corrected for estimated changes in bond lengths. In that case, no unpaired spin density appears on the hydrazine nitrogen atoms of the dinitro-substituted hydrazyl at all—the unpaired electron is confined to the aromatic rings. All of the wave functions from the Streitwieser parameters differ from those obtained with other parameters in that the unpaired electron has about two times higher probability on the atoms of each of the two *o*-nitro groups of the picryl rings than on those of the *p*-nitro group.

After a series of calculations with these and other more or less arbitrary parameters, the systematic methods for estimating coulomb and exchange integrals were developed. The computations for the hydrazyls with these parameters still fail to reproduce all details of the changes in spin density with substitutions. In particular, the increase in ρ_{13} when substituent nitro groups are present does not appear in the computed results. Variations of the systematic parameters were then undertaken in order to find a combination which would produce this increase. It turns out that no adjustment of a single parameter is adequate; in fact, $\alpha_1 = \alpha_{10}$, α_{13}, and α_{14} all require adjustment. After these changes, the increase in ρ_{13} is obtained, but the small decrease in ρ_{14} is lost. Individual values of ρ_{13} and ρ_{14} are almost certainly too low. At the same time, the computed ratios ρ_{13}/ρ_{14} are quite close to the observed ratios a^{13}/a^{14}. Additional adjustments of the rotational angles φ (to 0°) and τ (to 27°) gave computed spin density ratios almost identical numerically with the ratios of the observed coupling constants. These results are collected in Table II, together with the experimental values from Chen, Sane, Walter, and Weil.[24] Again, it should be emphasized that ρ_i and a^i are *not* the same quantity, and that the relationship between them varies for atoms at different sites in these molecules. In fact, suitable adjustments of the input parameters will give a wide range of ρ_i values.

The parameters optimized for the hydrazyl computations give results inferior to those obtained with the systematic parameters when applied to the triarylmethyl radical series. That is, one expects (by analogy with the data for the triarylaminium radicals) that the C_0 spin density should decrease in roughly similar amounts when triphenylmethyl is substituted by either of the substituents considered. In fact, the change is larger by an order of magnitude for nitro substitution.

The calculated optical spectra are also better for the hydrazyl series. The data in Table III show that all parameters except Streitwieser's reproduce the observed blue shift for substitution by OCH_3, and the red shift for NO_2 substitution. In all cases, far the lowest energy transition involves excitation of the unpaired electron to the next higher MO, rather than an electron from a fully occupied MO to that which is half filled. The "optimum" parameters give bonding MO for both states involved in the transition; other parameters make one or both of these antibonding. As in the case of the spin densities, the results are not as good for the triarylmethyl radicals. The observed (or expected) red shift is predicted for all cases, but the magnitude is much too large for the nitro-substituted radical. The energy differences are such that the lowest energy transition for the nitro-substituted compound involves excitation of the unpaired electron to the lowest (empty) antibonding MO. That for the methoxy-substituted compound involves excitation of one electron (of a pair) to the MO occupied by the unpaired electron. Within the precision of the MO treatment, these two possible transitions involve equal energies in triphenylmethyl itself.

Table III. Computed Energies of Longest Wavelength Absorption Bands in Optical Spectra of Two Types of Free Radicals

Radical	Exptl maxima, cm^{-1} $\times 10^{-4}$	Bersohn	Streitwieser	Systematic	"Optimum"
Dinitrohydrazyl	2.06[a]	0.388	0.048	0.119	0.108
Unsubstituted hydrazyl	1.92[a]	0.317	0.026	0.113	0.095
Dimethoxy-hydrazyl	1.78[a]	0.230	0.030	0.110	0.091
Tris(*p*-nitrophenyl)methyl	1.53[b]	0.574	0.112	0.153	0.080
Triphenylmethyl	1.97[b]	1.000	1.000	1.000	1.000
Tri-*p*-anisylmethyl	. . .[c]	0.689	0.898	0.888	0.888

[a] See ref 2. [b] See G. N. Lewis, D. Lipkin, and T. Magel, *J. Am. Chem. Soc.*, **66**, 1579 (1944). [c] No data are available on this compound. The value should be less than that for triphenylmethyl; see ref 2.

The good (if artificial) correspondence between ρ_{13}/ρ_{14} and a^{13}/a^{14} with the "optimum" parameters encourages the expectation that these parameters might also predict the relative values of the coupling constants for other radicals of the hydrazyl type. The results for a series of these compounds are given in Table IV, with the available experimental data. The calculations for the first three compounds in Table IV require no parameters in addition to those listed in Table II, and the calculated ratios ρ_{13}/ρ_{14} correspond surprisingly well with the experimental a^{13}/a^{14} ratios. The calculated spectral shifts (relative to the unsubstituted compound at 1.92×10^4 cm^{-1}, or 0.095β) do not turn out as well. Compounds four through seven each require one additional parameter for the bonds between aromatic rings, and the fit of the computed results to the observed $a^{13}a^{14}$ is not as close. Calculations for compounds five and seven through eleven are predictions for which no data are now available as checks. Probably the calculated results for 1-benzoyl-2,2-diphenylhydrazyl are poorest (this is certainly true for ΔE), since the largest number of additional parameters is required in that case. We are preparing the compounds in which one or more picryl ring nitro groups are replaced by hetero nitrogen in order to determine their properties.

One feature of these calculations which evidently has not been used previously is the interaction of the picryl ring with two orthogonal AO's on atom 13. The initial hope was that the calculations would reveal large changes in the π-electron energy of the hydrazyl system with change in φ, and thus establish this aspect of the molecular conformation. The effect of this variable depends upon the values assigned to the other parameters (this is true in general for variation in any single parameter, or group of them), but in no case has there been a large effect of φ upon π bond energy. With the "optimum" values of all other parameters, the π bond energy decreases about 0.2β (the total is 40.40β at $\varphi = 0°$) as φ increases from 0 to 90°. Thus the conformation with $\varphi = 0°$ is favored by a number of kilocalories (depending upon the value selected for φ) if steric factors are ignored. When φ is increased, the values of the individual spin densities at atoms 13 and 14 increase severalfold, and ρ_{13}/ρ_{14} increases more slowly from 1.26 to 1.89, as the unpaired electron

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(24) See Table II, footnote *c*.

Table IV. Computed Parameters for Various Hydrazyl Derivatives

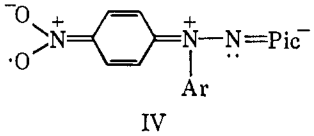
Compound: Rings attached to N_{14}	Compound: Ring attached to N_{13}	Calcd spin densities: Atom	Calcd spin densities: Value	Observed coupling constants, oersteds	Calcd ΔE, β	Obsd ΔE, $\text{cm}^{-1} \times 10^{-4}$
4-Nitrophenyl, phenyl	Picryl	13	0.197	10.43		
		14	0.134	6.95	0.103	...
		13/14	1.47	1.50[a]		
Phenyl	2,4-Dinitrophenyl	13	0.197	9.49		
		14	0.140	6.74	0.079	1.90[c]
		13/14	1.41	1.41[b]		
Phenyl	2,6-Dinitrophenyl	13	0.192	10.38		
		14	0.135	7.16	0.080	1.99[c]
		13/14	1.42	1.45[b]		
p-Biphenylyl	Picryl[d]	13	0.184	9.51[e]		
		14	0.146	7.51	0.094	1.82[c]
		13/14	1.26	1.27[a]		
3,6-Dinitro-9-carbazyl	Picryl[f]	13	0.239	...		
		14	0.119	...	0.121	...
		13/14	2.01	...		
9-Carbazyl	Picryl[f]	13	0.233	...		
		14	0.138	...	0.111	...
		13/14	1.69	2.00[g]		
3,6-Dimethoxy-9-carbazyl	Picryl[f]	13	0.221	...		
		14	0.139	...	0.107	...
		13/14	1.59	...		
Phenyl	3,5-Dinitro-2-pyridinyl[h]	13	0.211	...		
		14	0.154	...	0.085	...
		13/14	1.57	...		
Phenyl	3,5-Dinitro-4-pyridinyl[h]	13	0.205	...		
		14	0.149	...	0.086	...
		13/14	1.38	...		
Phenyl	5-Nitro-2-pyrimidyl[h]	13	0.234	...		
		14	0.163	...	0.131	...
		13/14	1.44	...		
Phenyl	Benzoyl[i]	13	0.314	...		
		14	0.305	...	0.592	1.97
		13/14	1.23	...		

[a] From Table II, footnote *c*. [b] From (a) A. T. Balaban, M. Marculescu, I. Pascaru, M. Rotaru, A. Valeriu, and M. Wiener, *Z. Physik Chem.* (Leipzig), **219**, 285 (1962); (b) B. M. Kozyrev, Yu. V. Yablokov, R. O. Matevosian, M. A. Ikrina, A. V. Iljasov, Yu. M. Ryshmanov, L. I. Stashkov, and L. F. Shatrukov, *Opt. i Spektroskopiya*, **15**, 625 (1963). [c] From A. T. Balaban, P.T. Frangopol, M. Marculescu, and J. Bally, *Tetrahedron*, **13**, 258 (1961). [d] The ring–ring bond is assumed to have the length 1.51 A (from A. Hargreaves and J. H. Rizui, *Acta Cryst.*, **15**, 365 (1962)), with $\beta = 0.71\beta_{cc}$. [e] From ref 2. [f] The ring–ring bond in the carbazole system is assumed to have the exchange integral $\beta = 0.78\beta_{cc}$. [g] From H. S. Jarrett, *J. Chem. Phys.*, **21**, 761 (1953). [h] For the hetero nitrogen atom, $\alpha_N = \alpha_C + 0.22\beta_{cc}$, and $\beta_{CN} = 0.77\beta_{cc}$. [i] The parameters used were $\beta_{C-C_6H_5} = 0.68\beta_{cc}$, $\beta_{CO} = 0.74\beta_{cc}$, and $\beta_{CN_{13}} = 0.58\beta_{cc}$. For the carbonyl oxygen, $\alpha_0 = 0.70$. [j] From W. K. Wilmarth and N. Schwartz, *J. Am. Chem. Soc.*, **77**, 4543 (1955).

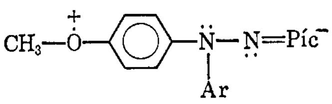
density on the picryl ring drops to zero. If steric requirements are considered, the *o*-nitro groups must be rotated out of the plane of the picryl ring when $\varphi = 0°$. If τ is taken as 30°, the π bond energy is decreased 0.06β, and the unpaired electron density of the *o*-nitro groups drops to about 80% of the value at the *p*-nitro group of the picryl ring. With another (arbitrary) set of parameters for the calculations, the π bond energy has a very shallow maximum (0.01β) at $\varphi = 55°$. It appears that π bond energy does not vary enough with φ to favor strongly a particular conformation of the free-radical system with respect to this angle.

There is some interest in examining the nature of the wave functions which are obtained from these calculations. Unpaired electron density is highest on the two hydrazine nitrogens, but it is probably too low, with the parameters chosen, to account for the observed coupling constants due to these atoms. (The wave function obtained with the Streitwieser parameters places most of the unpaired electron density on the nitro groups of the picryl ring.) It is also large on the three nitro groups of the picryl ring, with the probability about 2.5 times greater that it will be on the oxygen atoms than on the nitrogen. Elsewhere it is quite low, particularly in the two aromatic rings.

Substitution of nitro groups in the aromatic rings effects a partial shift of the unpaired electron from the nitro groups in the picryl ring to these new substituents, but the unpaired electron density is about three times greater on each of the former. The effect of introduction of nitro groups on this MO is similar to that expected from a contribution of VB structures like IV to the resonance hybrid for the substituted radical.



IV



V

Substitution of methoxy groups in these positions effects a substantial redistribution of the unpaired electron by withdrawing it from atom 13, and simultaneously increasing slightly the spin density at all positions on the picryl ring. There is little change in the two aromatic rings, and almost no ($\rho_{28} \sim 0.002$)

probability that it will be found on the oxygen atoms of the methoxy groups. This is contrary to the expectation that VB structures like V should contribute substantially to the resonance hybrid for this molecule.[2]

There is also interest in examining the distribution of unshared electron pairs in these systems. Wave functions obtained with the "optimum" parameters (which used $\varphi = 0°$, and $\tau = 27°$) include one in which an electron pair has a high probability ($\rho_{13} = 0.100$, $\rho_{14} = 0.185$) that it will be on atoms 13 and 14, and is otherwise distributed among the *ortho* and *para* positions of all three aromatic rings. A strongly bonding MO contains one electron pair fully localized on AO no. 27. These results are not changed by either type of substitution studied. Somewhat different results are obtained when $\varphi = 45°$. The unpaired electron distribution is essentially unchanged, with some increase in density at atoms 13 and 14, at the expense of density on the nitro groups in the picryl ring. An unshared electron pair has substantial probabilities in AO no. 14 and 27, with distribution otherwise to *ortho* and *para* positions of all three rings. A strongly bonding MO has nearly half of the electron density in position 27, and the remainder in the picryl ring. These distributions are not greatly affected by substitution.

Mass Spectrometry in Structural and Stereochemical Problems. CIV.[1] The Nature of the Cyclic Transition State in Hydrogen Rearrangements of Aliphatic Sulfides[2]

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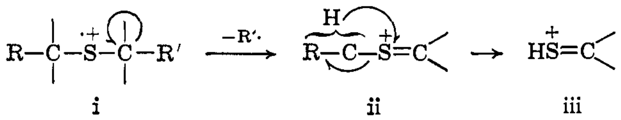
Contribution from the Department of Chemistry, Stanford University, Stanford, California. *Received December 22, 1965*

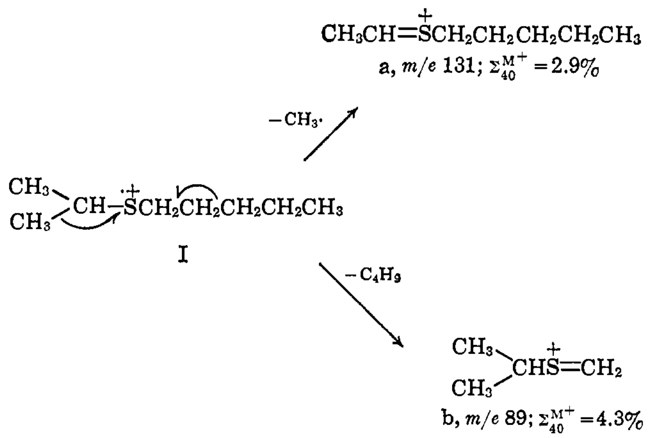
Abstract: Levy and Stahl[4] first studied the fragmentation of thioethers and concluded that the spectra were dominated by fragments arising from α cleavage, carbon–sulfur cleavage, and olefin elimination forming mercaptan ions. A fourth type of fragmentation, characteristic of ethers and amines, is also found and is represented below for the sulfur case. Through deuterium-labeling experiments, it has now been demonstrated that the hydrogen transfer to



sulfur (ii → iii) is not just a four-centered process as had been originally postulated[5] for formation of the analogous fragment in ethers. Rather as had been shown recently with labeled ethers[6a] and amines,[6b] four-, five-, and six-membered cyclic transition states transferring secondary hydrogen to sulfur are equally favored. However, if a choice between secondary and primary hydrogen is available, transfer of the former predominates. Other features of the mass spectra of aliphatic sulfides, including those observed by Levy and Stahl,[4] are discussed in terms of deuterated analogs.

A preliminary study of the fragmentation of thioethers upon electron bombardment was made by Levy and Stahl[4] in 1961. They observed that the spectra were dominated by fragments arising from α cleavage, carbon–sulfur bond cleavage, and olefin elimination to form mercaptan ions.

The first of these processes, α fission, is also important in the fragmentation of ethers[5,6a] and amines.[6b,7] Its counterpart in sulfides can be illustrated by the mass spectrum (Figure 1) of isopropyl *n*-amyl sulfide (I). It should be noted that the usual mass spectrometric generalization holds, namely, that the more highly substituted radical is lost preferentially.[5,8] However,



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[3] Recipient of National Science Foundation (1963–1965) and National Institutes of Health (1965–1966) predoctoral fellowships.

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