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LCAO–MO CALCULATIONS ON VERDAZYLS*

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Abstract—Simple Hückel MO theory satisfactorily explains several experimental results, amongst them the near equivalence of the four nitrogen atoms, whose hyperfine coupling constants are identical at least within the resolution of the spectra, as determined by the linewidths. The biradicals III and IV and the triradical V have a node in the odd electron orbitals at the aryl system connecting the radical parts and should consequently exhibit little intramolecular spin exchange. The same result can be derived from polarographic experiments and the broadening of lines in the ESR spectra can be attributed mainly to dipol-dipol interaction, not electron exchange. In contrast to the radicals III to V, in which the unpaired electrons occupy energetically degenerate orbitals, the radical electrons in VI occupy closely neighboring levels. The temperature-dependent paramagnetism of this substance results from the temperature-dependent population of these two levels. The calculated bond orders and charge densities show a delocalization of the remaining π-electrons over the whole molecule. Optical spectra cannot be interpreted within the HMO theory.

KUHN AND TRISCHMANN[1] have synthesized a series of remarkably stable, nitrogen-containing free radicals, which they named verdazyls. Measurements with a Gouy-Balance showed the presence of one unpaired electron (UPE) per molecule. The ESR spectra are characterized by nine lines of intensity 1:4:10:16:19:16:10:4:1, and hence show that the four nitrogen atoms must possess nearly identical spin densities. The combination of two or even three verdazyl systems yielded bi- and triradicals.[2] These molecules have similar properties as the simple verdazyls, and the ESR spectra indicate a weak interaction only between the unpaired electrons. All of the biradicals, with the exception of VI, retain their full paramagnetism upon lowering the temperature to 77°K.

The purpose of the present communication is the calculation of diverse properties of the verdazyls, such as spin density distribution, charge densities, bond orders, bond lengths, and optical transitions, and a comparison of the calculated properties with experimental data.

The method employed is the simple Hückel LCAO–MO theory. The following molecules are treated:

I: 1,5-diphenyl-verdazyl,
II: 1,3,5-triphenyl-verdazyl,
III: 1,4-bis-[1,5-diphenyl-verdazyl-3-yl]benzene,
IV: 1,3-bis-[1,5-diphenyl-verdazyl-3-yl]benzene,
V: 1,3,5-tris-[1,5-diphenyl-verdazyl-3-yl]benzene, and
VI: 4,4'-bis-[1,3-diphenyl-verdazyl-5-yl]biphenyl.

* On verdazyls Part 12; Part 11: R. Kuhn, F. A. Neugebauer and H. Trischmann, *Mh. Chem.* in press.

[1] R. Kuhn and H. Trischmann, *Angew. Chem.* 75, 294 [1963]; *Mh. Chem.* 95, 457 [1964].

[2] R. Kuhn, F. A. Neugebauer and H. Trischmann, *Angew Chem.* 16, 230 (1964); 16, 691 (1964); 17, 43 (1965); *Mh. Chem.* 97, 525 (1966).

Method. The simplest of the π-electron theories is due to Hückel.[3] Because of the size of the molecules being investigated, a factorization of the secular determinant is useful. If one assumes a planar configuration of the atoms, the molecules possess the following symmetries, and the MO's can be classified into the irreducible representations shown below. The degeneracy of each representation gives the size of the eigenvalue matrix which must be solved.

Radical	Symmetry	Irr. Representation I'
I	C_{2v}	$8\,A_2 + 9\,B_2$
II	C_{2v}	$10\,A_2 + 13\,B_2$
III	D_{2h}	$9\,A_u + 9\,B_{2g} + 11\,B_{2g} + 11\,B_{1u}$
IV	C_{2v}	$19\,A_2 + 21\,B_2$
V	D_{2h}	$8\,A_1'' + 11\,A_2'' + 19\,E''$
VI	C_{2v} or	$23\,A_2 + 23\,B_2$ or
	C_{2h}	$23\,A_u + 23\,B_g$

Because of the symmetry properties of the $2p_z$ atomic arbitals, only representations which are antisymmetric w.r.t. reflection in the molecular plane can occur.

The secular determinants contain only the coulomb integral α_r and the exchange integral β_{rs}, where the latter is only defined for neighbouring atoms. If the molecule contains heteroatoms, the Coulomb integral is modified to

$$\alpha_r' = \alpha_r + h_r\beta_{cc} \tag{1}$$

while the exchange integral is changed to

$$\beta_{rs}' = k_{rs}\beta_{cc} \tag{2}$$

Values of α_r' and β_{rs}' for various atoms and pairs of atoms vary considerably (4), and a choice within certain limits is quite arbitrary. Since the experimentally determined nitrogen hyperfine coupling-constants a_N are known from ESR spectra, a comparison with semiempirically calculated a_N is possible. The calculation of nitrogen coupling constants is based on the C^{13}-theory of Karplus and Fraenkel;[5] in particular, Stone and Maki[6] have suggested the equation

$$a_N = \left(S^N + \sum_i Q^N_{NX_i}\right)\rho_N^\pi + \sum_i Q^N_{X_iN}\rho^\pi_{X_i} \tag{3}$$

where the first term on the right-hand side of (3) gives the contribution of electron spin density in the nitrogen $2p_z$ orbital, the second summation the contributions of spin densities on the i neighbouring atoms. The spinpolarization parameters have been discussed in several papers. They are dependent on the type of MO calculation and the parameters employed therein. To be able to use known polarization parameters,[6] k_{CN} and h_N were set equal to 1·2; these same values have been used by Stone and Maki. A determination of spinpolarization parameters for the verdazyls was not undertaken, since the equation for determination of same would be nearly linearly dependent. β_{NN} was put equal to β_{cc}, in accordance with calculations of Rasch[7] and others.[8]

[3] E. Hückel, *Z. Physik.* **70**, 204 (1931).
[4] A. Streitwieser, *M.O. Theory for Organic Chemists.* Wiley, N.Y. (1961).
[5] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.* **35**, 1312 (1961).
[6] E. W. Stone and A. H. Maki, *J. Chem. Phys.* **39**, 1635 (1963).
[7] G. Rasch, *Z. Chem.* **2**, 347 (1962).
[8] G. Favini, I. Vandoni and M. Simonetta, *Theoret. Chim. Acta* **3**, 45, 418 (1965); **2**, 116 (1964).

Each carbon atom (excepting that of the CH_2-bridge) contributes one π-electron to the π-system of the radical, while two nitrogens contribute one, the remaining two nitrogens two π-electrons. An sp^2-hybridization of all the heavy atoms is assumed, with the exception of the methylene bridge carbon. It was not included in the calculations, as the interaction of the CH_2 protons with the π-system, hence the interaction of the CH_2 carbon, can be neglected, as shown by the vanishingly small coupling constants of the protons.[15]

RESULTS AND DISCUSSION

(1) *Energy levels and optical transitions.* Figure 1 shows the orbital energies of the six verdazyls in units of $|\beta|$. An excited state can be approximated if one assumes that an electron is promoted to an orbital, which in the ground state is either empty or singly occupied. The required energy of this transition is given, within the framework of the Hückel approximation, by Eq. 4:

$$E_K - E_J = (m_K - m_J)\beta \tag{4}$$

The energies of the lowest energy transitions of the six verdazyls are given in column 2 of Table 1, while the energy differences between the singly occupied orbitals and the fully occupied orbital directly below are listed in column 3. The last column contains the ratio of these two quantities, and should, if Eq. 4 is valid, be a measure of $|\beta|$.

TABLE 1. LOWEST ENERGY TRANSITIONS OF THE VERDAZYLS I–VI

Radical	Energy (cm^{-1})	Energy diff. (β)	$\lvert\beta\rvert$ (cm^{-1})
I	14·925	0·3259	45·796
II	13·889	0·2975	46·686
III	13·661	0·2576	53·032
IV	13·908	0·2866	48·528
V	13·870	0·1940	71·495
VI	13·123	0·1756	74·732

If one takes electron correlation explicitly into account, as in the PPP-theory for instance,[9] the integrals β are complicated functions of the electron-repulsion and core integrals, not a characteristic integral for a given C—C bond. Consequently the value of β should be a function of molecular geometry, and vary accordingly.

Even for closely related molecules as I to VI, β is not constant, but increases with increasing size of the molecule. The average value of $\beta = 7{\cdot}03$ eV $= 162$ kcal $mole^{-1}$ bears no relation to values obtained with other methods, experimental or computational. Even with the above value of β an interpretation of the optical spectra is not possible. These can presumably be explained only after inclusion of extensive configuration interaction, especially in the case of the bi- and triradicals, in which energetically degenerate or very closely neighbouring orbitals are found.

Figure 1 shows that the unpaired electrons of radicals III, IV and V occupy completely degenerate orbitals, while in VI two closely spaced energy levels harbour the UPE. The energy difference between these two orbitals is $0{\cdot}1338\beta$ or approximately 3 kcal $mole^{-1}$, if a conventional value of β is used. This energy difference,

[9] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).

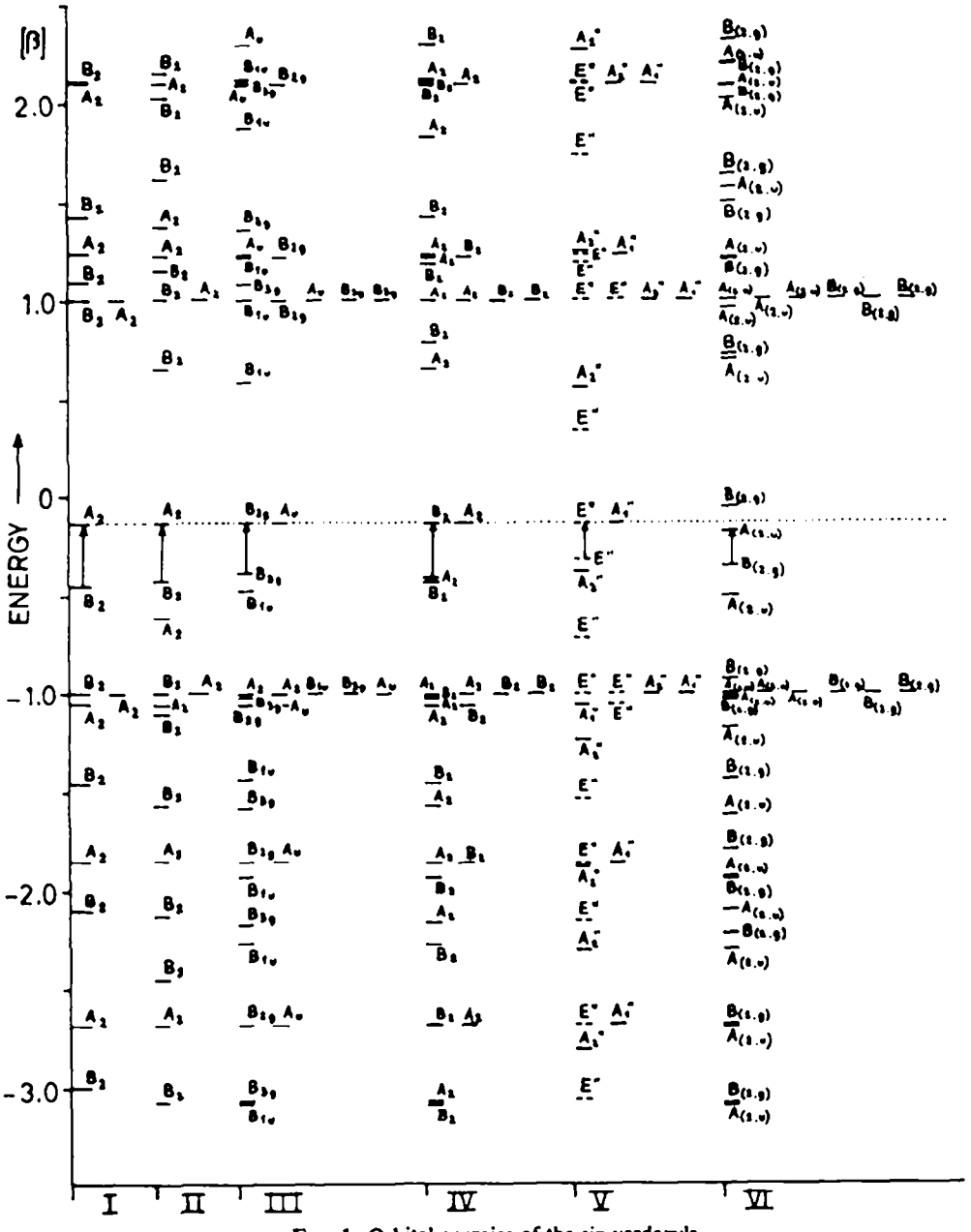


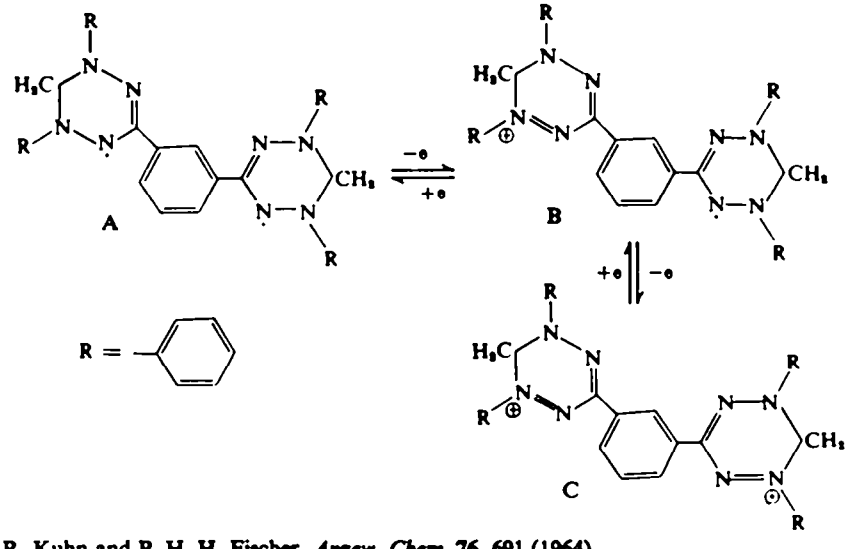
FIG. 1. Orbital energies of the six verdazyls.

which must of course be regarded as a coarse approximation, is of the same order of magnitude as kT. The decreasing paramagnetism[8] with falling temperature can consequently be explained by the temperature dependent population of these two levels. From the decrease of the paramagnetism, the energy difference ΔE has been determined as 0·85 kcal mole^{-1}.[8]

(2) *Electronic interaction.* As can be seen in Fig. 2, the orbitals containing the UPE of radicals III, IV, and V, have, at least in the Hückel approximation, a node in the benzene rings which connect 1,5-diphenyl-verdazyl systems. One could think of the unpaired electrons as being contained in potential wells, whose spatial expansion does not reach beyond the 1,5-diphenyl-verdazyl units. In biradical VI the orbitals containing the UPE are distributed over the whole molecule and thus lead to a stronger interaction of the odd electrons. In the McLachlan approximation, the orbitals are spinpolarized so as to yield nonvanishing spin densities in the central benzene rings of radicals III to V. These spin densities are however still quite small and electron interaction should still be considerable less than in radical VI.

All of the bi- and triradicals of this series show less well resolved ESR spectra than the monoradicals 1,5-diphenyl-verdazyl or 1,3,5-triphenyl-verdazyl. The most probable reason for the decreased resolution is the electron-electron interaction, although a poorer averaging out of anisotropic hyperfine interactions as consequence of the larger molecular size and hence increased correlation time, should perhaps not be disregarded. In the case of broadening due to electronic interaction, it remains questionable whether dipol–dipol interaction, electron exchange, or a combination of both, are responsible. In the ESR spectra of the bi-radicals, a hyperfine interaction with four nearly equivalent nitrogen nuclei seems indicated, although this observation is to be interpreted cautiously because of the poorer resolution. If interaction with four nitrogens only is indeed present, then the frequency of spin exchange $1/\tau_e$ would be much smaller than the hyperfine coupling a_N', i.e. $1/\tau_e \ll a_N' \simeq 10^7$ sec^{-1}.

The following reversible reactions, illustrated on the radical 1,3-bis-[1,5-diphenyl-verdazyl-3-yl]benzene, may be effected on substances III, IV, and V:[10]



[10] R. Kuhn and P. H. H. Fischer, *Angew. Chem.* 76, 691 (1964).

Through stepwise polarographic oxidation the biradical A can be converted to the monoradical B, then to the diamagnetic dication C. The oxidation A $\xrightarrow{-e}$ B is accompanied by a gradual improvement in the resolution of the ESR spectrum, until a well resolved spectrum, completely identical with the spectra of I or II, is obtained. The improved resolution is consequently attributable to the lack of electron-electron interaction. Furthermore it shows with certainty that the UPE interacts only with the

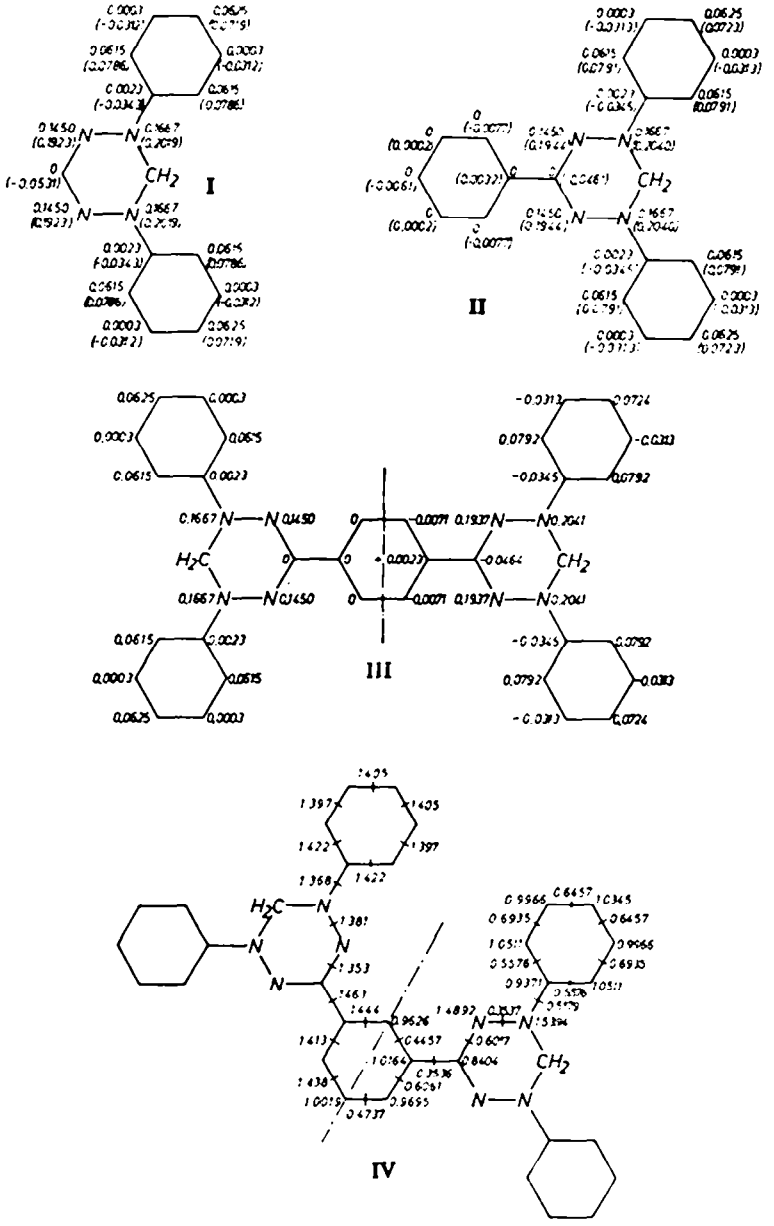


FIG. 2. Hückel and McLachlan spin densities of radicals I to VI.

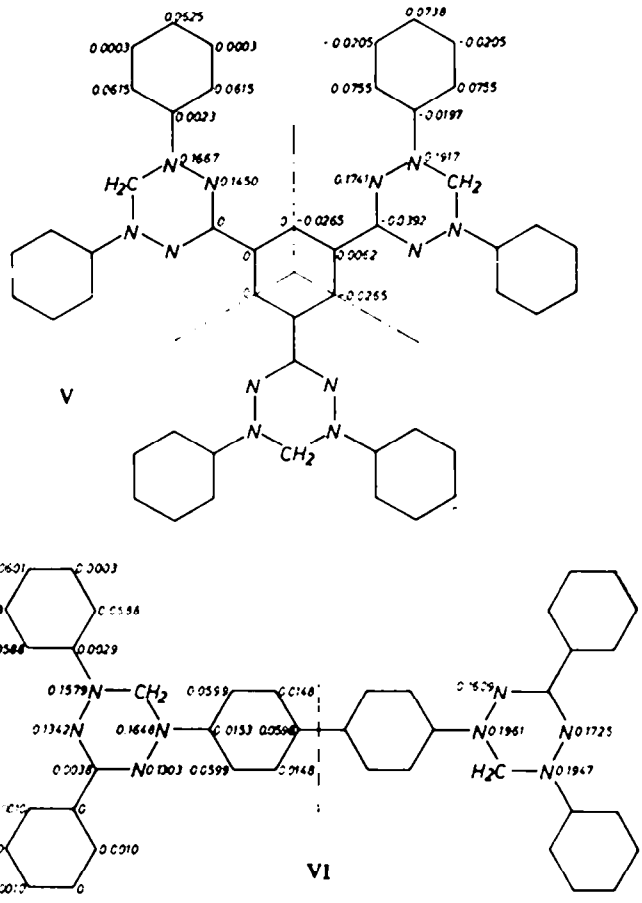


FIG. 2 (*cont'd*)

magnetic nuclei of one half of the radical B, as otherwise at least 17 or 25 lines should be present in radicals III and IV or V, corresponding to an interaction with 8 or 12 nearly equivalent nitrogen nuclei. The frequency of electron tunnelling $1/\tau_T$ from one potential well (i.e. radical site) to the other is thus, at least for the case of monoradicals derived from radicals III to V, decidedly slower than 10^7 sec^{-1}, i.e. $1/\tau_T \ll 10^7$ sec^{-1}. One cannot definitely say anything about the relation of $1/\tau_e$ to $1/\tau_T$ but it is probable that $1/\tau_e < 1/\tau_T$.[11] This reasoning corroborates the apparent observation that the UPE interact with only nitrogen nuclei of their own potential well in the biradical systems.

It has been thus shown, that the broadening of the ESR-lines of the bi- and triradicals III to V is primarily due to an interaction of the unpaired electrons. Furthermore, a differentiation between dipolar and exchange broadening is possible. The relationship $1/\tau_e < 1/\tau_T \ll a_N' \simeq 10^7$ sec^{-1} would seem to indicate that the major contribution to the broadening of the ESR lines of III to V is of the dipol–dipol type.

In biradical VI a different situation is apparent. A better resolution of the ESR

[11] A. I. Burshtein and Yu. I. Naberukhin, *Dokl. Akad. Nauk SSSR* **140**, 1106 (1961).

through polarographic oxidation could not be obtained; merely a decrease in intensity to complete disappearance of the spectrum was observed. Upon reduction, the original spectrum could not be regenerated.

(3) *Spin density distribution and coupling constants.* Figure 2 shows the calculated spin densities, either on the left side of the diagram, or as the first, unbracketed number for I and II. If one takes the equation of Atherton *et al.*[13] for the calculation of nitrogen coupling constants (this equation being used as the parameter of the spinpolarisation $Q_N^N = 28{\cdot}5$ Gauss was calculated with Hückel MO's), the following a_N are calculated.

TABLE 2. NITROGEN HYPERFINE COUPLING CONSTANTS (HMO)

Radical	ρ_{N_1}	a_{N_1} (theor.) [G]	a_{N_1} (obs.) [G]
I	0·1667	4·22	
			6·0 (Benzene)
	0·1450	3·67	
II	0·1667	4·22	
			5·98 (Benzene)
	0·1450	3·67	
III	0·1667	4·22	
			5·8 (Benzene)
	0·1450	3·67	
IV	0·1667	4·22	
			5·9 (Benzene)
	0·1450	3·67	
V	0·1667	4·22	
			not resolved
	0·1450	3·67	
VI	0·1648	4·17	
	0·1579	3·99	
			5·8 (Benzene)
	0·1342	3·40	
	0·1303	3·30	

All the values for a_N calculated with this parameter are too small. Other equations which are based on the HMO theory (see for example Ref. 13) yield equally poor agreement. Furthermore, the coupling constants for *o*-, *m*-, and *p*-protons of the N-phenyls, calculated via the McConnell Eq. 14 with $Q_{CH}^{H} = -23{\cdot}7$ G[5] are $a_{H_o} = 1{\cdot}46$ G, $a_{H_m} = \sim 0$ G, $a_{H_p} = 1{\cdot}48$ G. The Hückel spin densities at other carbon atoms having neighbouring hydrogens are zero. Since the hyperfine structure of the verdazyls I and II was not resolved beyond the nitrogen coupling, a direct comparison of calculated and experimental a_{H_1} was not possible. For the few compounds listed

[13] N. M. Atherton, F. Gerson, and I. N. Murrell, *Mol. Phys.* **5**, 509 (1962).
[5] J. C. M. Henning, *Academisch Proefschrift*. Amsterdam (1964).
[14] H. M. McConnell, *J. Chem. Phys.* **24**, 633, 764 (1956).

in Table 3, a complete analysis of the ESR spectra was however possible,[15] and gave the following coupling constants;

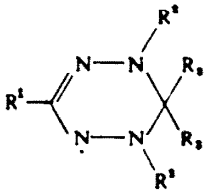
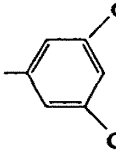
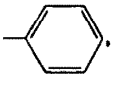
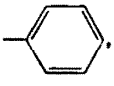
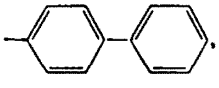
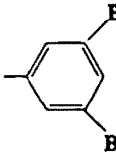


TABLE 3. PROTON COUPLING CONSTANTS OF SUBSTITUTED VERDAZYLS

Radical	$a_N(x)$	$a_N(y)$	$a_H(o)$	$a_H(m)$	$a_H(p)$
$R^1 = C_6H_4OC(=O)-$, $R^3 =$  , $R^5 = H$	5·82	5·82	1·09	—	1·09
$R^1 = C_6H_4OC(=O)-$, $R^3 =$  , $R^5 = H$	6·34	5·75	1·09	0·49	1·09
$R^1 = C_6H_4OC(=O)-$, $R^3 =$  , $R^5 = D$	6·34	5·75	1·09	0·47	1.09
$R^1 =$  , $R^3 =$  , $R^5 = H$	5·97	5·41	1·08	—	1·08

The agreement of the above *o*-, and *p*-proton coupling constants with calculated values is acceptable within the HMO approximation, the *m*-proton coupling constants however are unsatisfactory. Such a result is often observed in aromatic radical anions and cations, and introduction of configuration interaction via the McLachlan method[16] may yield a satisfactory ratio of a_o to a_m and of a_p to a_m. In the McLachlan approximation Hückel orbitals are employed for electrons of β-spin, while for α-spin electrons orbitals are calculated in which all exchange integrals β_{rs} remain unchanged, the Coulomb integrals α_r however are modified to

$$\alpha_r' = \alpha_r + 2\lambda |C_{o,r}|^2 \beta \tag{5}$$

Here α_r is the Hückel Coulomb integral, $C_{o,r}$ are the LCAO coefficients of atoms r in the HMO of the unpaired electron, and λ is a constant, commonly set equal to 1·2. The spin density ρ_r at atom r is now given by

$$\rho_r = |C_{o,r}|^2 + \sum_i (|C_{i,r}|^2 - |C_{i,r}'|^2) \tag{6}$$

[15] F. A. Neugebauer, to be published.
[16] A. D. McLachlan, *Mol. Phys.* 3, 233 (1960).

where the primed and unprimed coefficients belong to orbitals of β and α spin respectively. The summation extends over all the filled orbitals. The spin densities calculated in this fashion are given in Fig. 2, on the right side for radicals III to VI, in brackets for substances I and II. As was to be expected, the zero spin densities of Hückel theory have disappeared, and the nitrogen spin densities are obtained considerably larger.

Stone and Maki[6] have obtained two equations for calculating nitrogen coupling constants of N-heterocycles employing McLachlan spin densities. These equations are

$$a_N = Q_N^N \rho_N \tag{7}$$

for p-diazines, and

$$a_N = (S^N + Q_{NC}^N)\rho_N + Q_{CN}^N \rho_C \tag{8}$$

for *o*-diazines.

In the above equations, $Q_N^N = 28{\cdot}6 \pm 2{\cdot}3$ G, $(S^N + Q_{NC}^N) = 21{\cdot}1 \pm 0{\cdot}46$ G, and $Q_{CN}^N = -2 \pm 2$ G, have their usual meaning. It is to be noted that Eq. 8 is only valid if two terms, namely $Q_{NN'}^N = -Q_{N'N}^N$, can be neglected, an approximation which is valid only of the neighbouring nitrogens are identical, i.e. have exactly the same spin density. It is difficult to decide which of the equations, if any, is to be applied to verdazyls. Table 4 gives the a_N which have been calculated employing both (7) and (8). The agreement with experimental values is for Eq. 8 not better than when employing HMO, however for Eq. 7 excellent agreement is observed, both as to the absolute value of a_N and the small difference between $a_N(x)$ and $a_N(y)$.

TABLE 4. CALCULATED NITROGEN COUPLING CONSTANTS (MCLACHLAN) SPIN DENSITIES

Radical	Position*	a_N(Eq. 8) [G]	a_N(Eq. 7) [G]
I	1	4·33	5·77
	2	4·17	5·50
II	1	4·37	5·83
	2	4·19	5·56
III	1	4·38	5·84
	2	4·18	5·54
IV	1	4·37	5·83
	2	4·19	5·56
V	1	4·08	5·48
	2	3·75	5·01
VI	1	4·22	5·61
	2	3·44	4·60
	3	4·19	5·57
	4	3·69	4·93

* The assignment of the a_N may be ascertained from Fig. 2.

The spin densities in the meta position of the N-phenyl rings has been modified to $\sim -0{\cdot}03$ by the spin polarization. The proton coupling constants which have been calculated employing McLachlan spin densities and $Q_{CH}^H = -23{\cdot}7$ G, are listed in Table 5. As for many aromatic radicals, one finds that the absolute value of a_H for *o*-, *m*- and *p*-protons is not reproduced better than with HMO theory, that the ratios a_o/a_m and a_p/a_m are however quite accurately given. Experimentally one finds for

several verdazyls that $a_{o,p}/a_m = 2{\cdot}27$ (see Table 3), while one calculates $a_o/a_m = 2{\cdot}53$ and $a_p/a_m = 2{\cdot}31$.

TABLE 5. CALCULATED PROTON COUPLING CONSTANTS (MCLACHLAN SPIN DENSITIES)

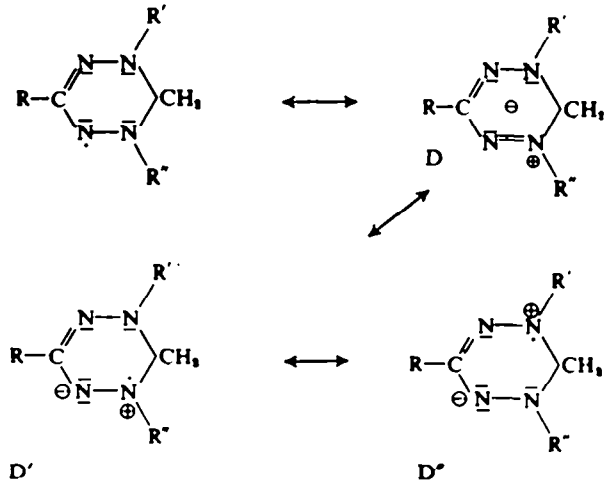
Radical	a_{ortho} [G]	a_{meta} [G]	a_{para} [G]
I	1·86	0·74	1·70
II	1·87	0·74	1·71
III	1·88	0·74	1·72
IV	1·88	0·74	1·71
V	1·79	0·49	1·75

(4) *Charge distribution, bond orders, and bond lengths.* The π-electron distribution q_r and the π bond orders P_{rs} of the six verdazyls I to VI are given in Fig. 3. They are calculated from the Hückel coefficients with the following equations:

$$q_r = 2\sum_i C_{ri}^2 + \sum_j C_{rj}^2 \tag{9}$$

$$P_{rs} = 2\sum_i C_{ri}C_{si} + \sum_j C_{rj}C_{sj} \tag{10}$$

The first summation extends over the i doubly occupied orbitals, while the second summation is over the j singly occupied MO's. In Fig. 3, the numbers at the atom coordinates represent the respective charge density, the number between atoms r and s the respective bond order P_{rs}, for substances III to VI on the right-hand side of the diagram. Especially noticeable is the charge density on the nitrogen atoms. The two nitrogen atoms neighbouring the methylene bridge, have an electron density which varies between 1·52 and 1·55, they have, since they both contribute 2 electrons to the π-system of the molecule, a net charge of +0·45 to +0·48. The two remaining nitrogen atoms show a similar charge density of 1·48 to 1·52, and a net charge of −0·48 to −0·52, since each of these atoms contributes only one electron to the π-system of the radical. The structure D formulated by Kuhn and Trischmann[1] seems thus plausible and may be more explicitly (D′ and D″) formulated as follows:



Since the overlap integral S_{rs} varies only slightly from one type of conjugated bond to another, the bond order is a good measure of the π-electron density in the bond region, and it should be possible to correlate bond order and bond length.

Various relationships between bond orders and length have been developed; in the present paper the formulae of Jenkins[17] have been employed. They are for CC-, CN- and NN-bonds:

$$\begin{aligned} r_e^{-2} &= 0{\cdot}2868 + 0{\cdot}1334P_{rs}^{CC} \\ r_e^{-2} &= 0{\cdot}316 + 0{\cdot}144P_{rs}^{CN} \\ r_e^{-2} &= 0{\cdot}263 + 0{\cdot}193P_{rs}^{NN} \end{aligned} \tag{11}$$

r_e denotes the equilibrium interatomic distance and P_{rs} is the total bond order, i.e.

$$P_{rs} = P_{rs}^{\pi} + P_{rs}^{\sigma} \tag{12}$$

The bond lengths which have been calculated using (11) are given in Fig. 3. All of the CC distances within the aromatic rings deviate only slightly from the aromatic CC bond length of 1·39 Å, while all of the CN bonds show considerable shortening when compared with the CN single-bond distance of 1·47 Å, in accordance with conjugation over the whole verdazyl-system, as expressed through structures D′ and D″. The lengths of CC bonds which connect 1,5-diphenyl-verdazyl systems to a common benzene ring, or the bond which in VI couples the 1,3,5-triphenyl-verdazyl

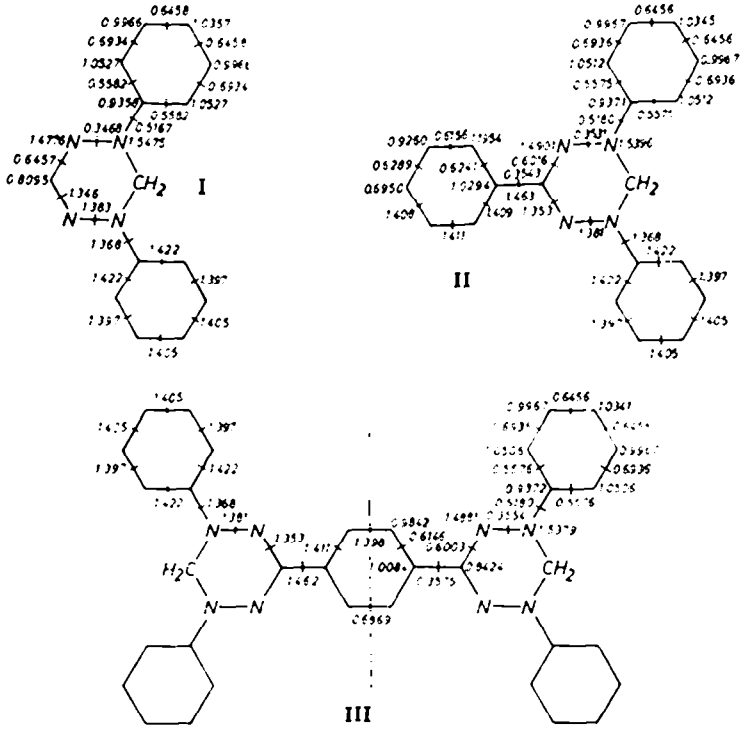
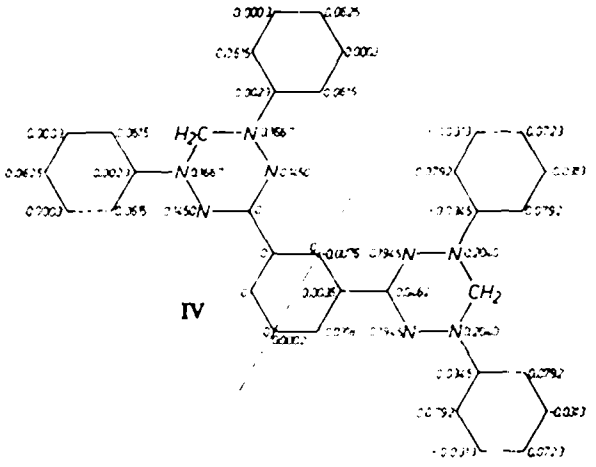
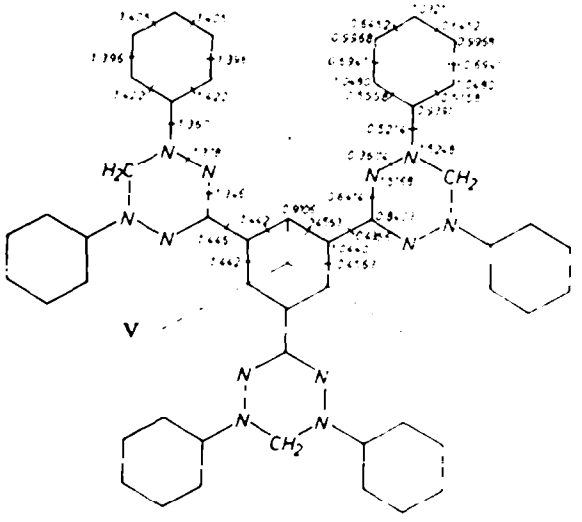


FIG. 3. Charge densities, bond orders, and bond lengths of radicals I to VI.

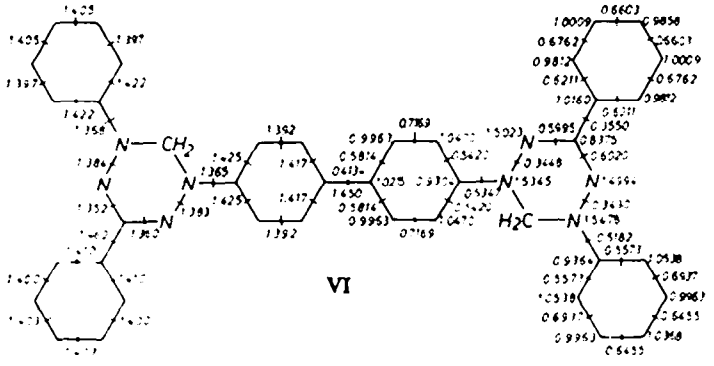
[17] H. O. Jenkins, *J. Am. Chem. Soc.* 77, 3168 (1955).



IV



V



VI

FIG. 3 (*cont'd*)

systems, range from 1·45 to 1·46 Å. They show a certain amount of double bond character, should however not completely prohibit rotation about these bonds. The diamagnetic form of VI would have a decreased connecting-bond length of 1·418 Å. Apart from the size of the molecule, it is also possible that a partial rotation about these bonds connecting radical-halves is responsible for the weak electronic interaction.

The simple MO theory, without mathematical refinements, often yields quite accurate values of interatomic distances, which are in no way inferior to values obtained via more elaborate methods. Unfortunately no crystallographic investigations of the verdazyls have been reported and a direct comparison of calculated and experimentally found bond lengths is impossible.

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