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Commentationes

Electronic Absorption Spectra and Dipole Moments for Hydrazyl Radicals

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The paper gives the results of the calculations of transition energies, dipole moments and bond lengths for some hydrazyl radicals carried out by the SCF LCAO MO method with restricted configuration interaction on self-consistent open-shell orbitals. The calculated transition energies for the radicals considered are in a good agreement with the locations of the long-range wave absorption maxima. It is shown that the DPPH dipole moment is the π-electronic moment. On introducing different substitutents in the molecule the σ-moment contribution may be quite considerable. The estimated values for the bond lengths in the substituted radicals show little alteration in the molecular structure.

Die Übergangsenergien, Dipolmomente und Bindungslängen einiger Hydrazylderivate wurden nach einem SCF-Verfahren mit Konfigurationswechselwirkung berechnet. Erstere sind in guter Übereinstimmung mit dem Experiment. Das Dipolmoment von DPPH ist gleich demjenigen der π-Elektronen, aber bei Substituenteneinführung kann das der σ-Elektronen einen beträchtlichen Beitrag liefern. Die Bindungslängen dagegen zeigen nur geringe Änderung.

Cet article donne les résultats de calculs d'énergies de transition, de moments dipolaires et de longueurs de liaison pour quelques radicaux hydrazyles calculés par la méthode SCF LCAO MO avec interaction de configurations limitée. Les énergies de transition calculées pour les radicaux étudiés sont en bon accord avec la position des maxima d'absorption de grande longueur d'onde. On montre que le moment dipolaire de DPPH est le moment électronique π. La contribution du moment σ peut devenir considérable par introduction de différents substituants. Les valeurs estimées pour les longueurs de liaison dans les radicaux substitués ne révèlent que peu de modifications dans la structure moléculaire.

Theoretical calculations of the absorption spectra for free radicals as well as of their dipole moments are of considerable interest in finding relations between the electronic structure and the properties of radicals.

For the first time calculations of absorption spectra for some hydrazyl radicals were carried out by Walter [1] by means of the Hückel MO method. However, their calculation and the strong dependence of the results on the values of the semiempirical parameters used did not allow to interpret the experimental spectra even qualitatively.

The present paper gives the results of calculations for α, α-diphenyl-β-picrylhydrazyl (DPPH) and some of its derivatives (Table 2) by the SCF MO LCAO CI method. Transition energies, dipole moments and bond lengths of these molecules have been estimated and comparison of the obtained characteristics with experimental data has been made.

Experimental Absorption Spectra for Hydrazyl Radicals

The electronic absorption spectra of benzene solutions of the radicals were taken by the spectrophotometers CF-10 and Spectromom-202. The parameters of the experimental absorption spectra are listed in Table 1. As an example, the experimental absorption curves for some investigated radicals are shown in Figs. 1a and 1b.

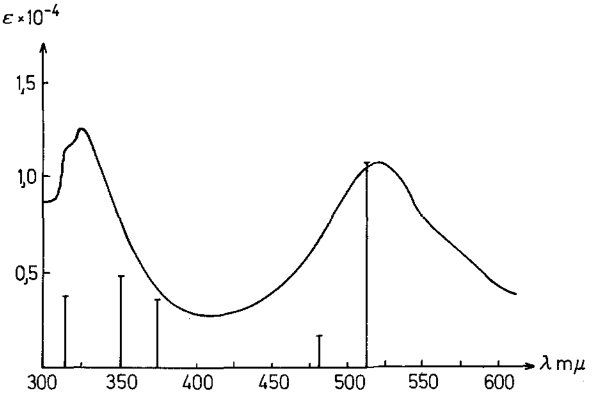

Fig. 1a

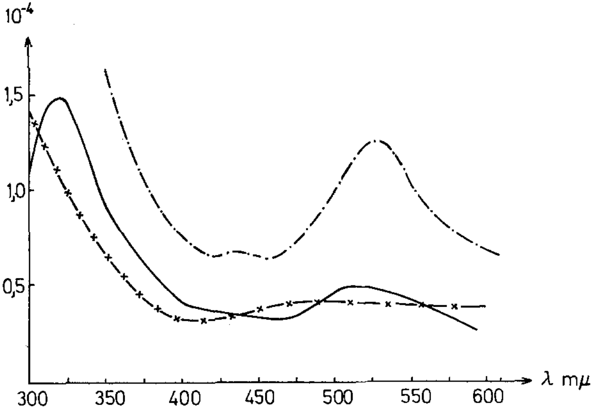

Fig. 1b

Fig. 1a and b. Electronic absorption spectra. a) DPPH with the calculated $\pi-\pi^*$-transitions. b) ——— α, α-diphenyl-β-2,6-dinitrophenylhydrazyl, —·—·— carbazylpicrylnitrogen, —×—×—× carbazyl-2,6-dinitrophenylnitrogen

Methods of Calculations.

Transition Energies of DPPH and its Dipole Moment

The calculations of the $\pi-\pi^*$ transition energies and of the π-electronic dipole moments of the radicals were carried out with the computer M-20. The computer program used permits to evaluate SCF MO's for the π-system of a radical [2] and to take account of singly excited configuration interaction[1].

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[1] Five doublet configurations are enclosed.

Table 1. *Resonance integrals* β_{rs}

Set	β_{rs} (eV)	β_{CC} (eV)
1	$-\frac{1}{2}(U_r+U_s)S_{rs}$	-2.37
2	$-\frac{1}{2}(U_r+U_s)S_{rs}$	-2.33
3	$-\frac{1}{2}(U_r+U_s)S_{rs}$	-2.39
4	$-\frac{1}{2}(U_r+U_s)\frac{S_{rs}}{1+S_{rs}}$	-2.33
5	$-\frac{1}{2}(U_r+U_s)\frac{S_{rs}}{1+S_{rs}}$	-2.39
6	$-0.437(U_r+U_s)S_{rs}$ [a]	-2.39
7	$-1.085\frac{(U_r+U_s)S_{rs}}{2(I+S_{rs})}$ [a]	-2.33

[a] Obtained from $\beta_{CC} = -2.39$ eV.

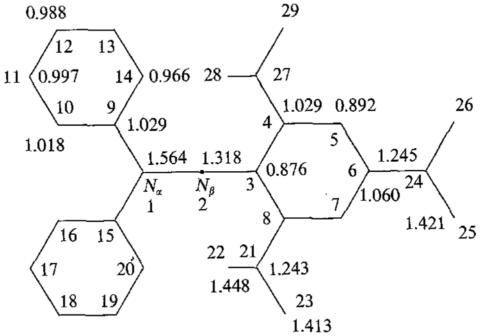


Fig. 2. Charge densities in α, α-diphenyl-β-picrylhydrazyl

Calculations of spin densities in hydrazyl radicals [3, 4] showed that the molecules are nearly planar while the β nitrogen atom has a *sp*-hybridization. The same type of molecule is dealt with in the present paper.

The semiempirical parameters used in the calculations are as follows:

1. ionization potentials and electron affinities as given in [5];
2. electronic interaction integrals as given in [6].

The calculations of the DPPH molecule were carried out with different values of resonance integrals β_{rs} (Table 1). Doublet-doublet and -quartet transition energies vary little when using different β_{rs}-sets. The dipole moments depend much more than the transition energies on the choice of the resonance integrals. The σ-dipole moment for DPPH calculated on the base of bond moments [7] is equal to zero. The best results (Table 2, 1) have been obtained with the first set of resonance integrals of Table 1. This one was also used in evaluating the substituted radicals (charge densities in DPPH for a particular β_{rs}-set are shown in Fig. 2). Fig. 1a also shows the locations of the calculated doublet-doublet transitions for DPPH. The first transition is the most intensive, its energy being close to the experimental value; in the UV area we found three transitions closely to one another.

The resonance integrals employed in the calculations of the spin distribution [3] (Table 1, 4) also gave reasonable results.

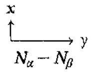
Table 2. *Transition energies and dipole moments for hydrazyl radicals*

No.	Radical	$\pi - \pi^*$-transition energies (eV) Doublet-doublet[a]	$\pi - \pi^*$-transition energies (eV) Quartet	Expt. absorption maximum (eV)	Dipole moments (D) π-moment	Dipole moments (D) Total moment[c]
1	2	3	4	5	6	7
1	DPPH (I)	2.433 2.576 3.288 3.528 4.005	3.200	2.39	5.25[d]	5.25
		(0.501) (0.072) (0.161) (0.205) (0.170)			(−)	(−)
2	α, α-diphenyl-β-2,6-dinitrophenylhydrazyl (II)	2.510 2.645 3.090 3.594 4.015	3.202	2.45	0.59	0.76
		(0.467) (0.100) (0.029) (0.086) (0.173)			(−)	(−)
3	α, α-diphenyl-β-2,4-dinitrophenylhydrazyl (III)	2.345 3.074 3.750 3.908 4.784	3.527	2.34[b]	6.45	5.29
		(0.419) (0.048) (0.041) (0.198) (0.102)			(−5.44)	(−4.76)
					(+3.47)	(+2.30)
4	α-4-nitrophenyl, α-phenyl-β-picrylhydrazyl (IV)	2.444 2.738 3.250 3.560 4.108	3.347		4.62	3.94
		(0.487) (0.094) (0.047) (0.212) (0.112)			(−1.86)	(−2.53)
					(4.23)	(+3.06)
5	α-biphenyl, α-phenyl-β-picrylhydrazyl (V)	2.368 2.530 3.337 3.498 3.896	3.235	2.35[b]	5.54	5.54
		(0.513) (0.074) (0.251) (0.212) (0.133)			(−5.54)	(−5.54)
					(+0.33)	(+0.33)
6	Carbazylpicrylnitrogen (VI)	2.265 2.325 2.885 3.707 4.090	3.364	2.35	3.62	3.51
		(0.021) (0.520) (0.103) (0.187) (0.069)			(−)	(−)
7	Carbazyl-2,6-dinitrophenylnitrogen (VII)	2.502 2.602 3.009 3.400 4.102	3.417	2.58	2.09	3.14
		(0.468) (0.017) (0.129) (0.014) (0.065)			(−)	(−)
8	3-Cl-carbazylpicrylnitrogen (VIII)	2.003 2.253 2.665 3.652 3.813	3.117	2.33	6.34	7.95
		(0.333) (0.230) (0.104) (0.202) (0.053)			(−6.13)	(−7.84)
					(+1.63)	(+1.34)

[a] Oscillator strengths are given in brackets.

[b] From Refs. [14, 16].

[c] Dipole moment polarization is indicated in brackets. Axis directions:



[d] Experimental dipole moment for DPPH: 4.92 D [15].

Dipole Moments and Absorption Spectra for Substituted Hydrazyl Radicals

The dipole moment for the radicals were evaluated as the sum of π-and σ-electronic moments. The latter was estimated on the base of bond moments [7] (C–Cl bond moment being taken to be equal to 1.5 *D* [8]). The lone pair electrons of the nitrogen atom which occupy the nonhybridized *p*-orbital, do not contribute to the σ-moment. The values of the π-electronic and the total dipole moments for the hydrazyl radicals are listed in Table 2. Experimental data concerning dipole moments for substituted hydrazyls are lacking in literature.

The energies for five doublet-doublet and the lowest quartet transitions are listed in Table 2. As in the DPPH case, calculations for substituted radicals yielded an intensive transition in the visible part of the spectrum and a number of transitions of much lower intensity in the UV area. In addition, for carbazylpicrylnitrogen (Table 2) there appears one more transition of low intensity in the long-range part of the spectrum.

Calculated values for the most intensive transition energies coincide with the experimental absorption maxima for hydrazyl radicals in the visible area (Table 2).

Bond Orders and Bond Lengths in Hydrazyl Radicals

The bond orders allow to estimate bond lengths in these radicals. For that purpose we used the relation [9]

$$R_{\mathrm{CC}} = 1.517 - 0.180 P_{\mathrm{CC}}\,, \tag{1a}$$

$$R_{\mathrm{CN}} = 1.541 - 0.180 P_{\mathrm{CN}}\,, \tag{1b}$$

$$R_{\mathrm{NN}} = 1.419 - 0.179 P_{\mathrm{NN}}\,, \tag{1c}$$

and [10]

$$R_{rs} = \sqrt{\frac{6{,}5}{Z_r + Z_s}}\,(1.523 - 0.190 P_{rs})\,. \tag{2}$$

Here P_{rs} is the bond order, Z_r and Z_s are Slater charges of atoms r and s. Eqs. (1 a) and (2) for C–C [(1 c) and (2) for C–N] bonds give identical results. The relation obtained from (2) for N–N bonds differs from (1 c):

$$R_{\mathrm{NN}} = 1.393 - 0.174 P_{\mathrm{NN}}\,. \tag{2a}$$

The bond orders and bond lengths in hydrazyl radicals calculated by means of Eqs. (1) and (2 a) are listed in Table 3. Those for DPPH agree with X-ray data for the crystalline radical [11]. The distortions of the DPPH molecule in crystal form seem to result mainly from alteration of the angles only.

According to the data obtained (Table 3), the geometry of the phenyl rings in hydrazyl radicals is a nearly rectilinear hexagon. The alternation of bond lengths which was found in some π-electronic radicals [12] has not been observed. The bond lengths for a hydrazyl fragment are invariable in all the radicals considered, which parallels with the little alteration in the spin polarization constants for the N_α and N_β atoms [3].

Refs. [9, 13] are concerned with the method of calculating the formation energies of conjugated molecules. The molecular energy of formation E is determined as

Table 3. *Bond orders and bond lengths* (Å) *in hydrazyl radicals*

Radical	Bond[a]													
	1–2	1–9	1–15	2–3	3–4	4–5	5–6	9–10	10–11	11–12	12–13	13–14	9–14	10–16
1	2													
DPPH[b]	1.33	1.41	1.43	1.37	1.41	1.40	1.38	1.41	1.39	1.38	1.35	1.38	1.39	
DPPH (I)	0.436	0.369	0.369	0.513	0.526	0.646	0.612	0.602	0.682	0.654	0.660	0.676	0.604	
	1.317	1.384	1.384	1.359	1,422	1.401	1,407	1.409	1.394	1.399	1.398	1.395	1.408	
	1.341[c]													
II	0.434	0.362	0.362	0.486	0.542	0.624	0.663	0.608	0.680	0.657	0.661	0.676	0.609	
	1.317	1.386	1.386	1.364										
	1.341[c]													
III	0.428	0.359	0.355	0.459	0.582	0.704	0.589	0.612	0.678	0.658	0.661	0.676	0.612	
	1.318	1.386	1.385	1.378										
		1.342[c]					(0.634)	(0.631)						
IV	0.436	0.363	0.364	0.497	0.534	0.644	0.615	0.604	0.682	0.655	0.661	0.676	0.607	
	1.317	1.386	1.386	1.362										
	1.341[c]							(0.599)	(0.693)	(0.610)	(0.614)	(0.685)	(0.603)	
V	0.435	0.374	0.370	0.516	0.524	0.647	0.612	0.597	0.691	0.624	0.630	0.685	0.599	
	1.317	1.384	1.385	1.358										
	1 341[c]							(0.602)	(0.682)	(0.655)	(0.660)	(0.676)	(0.604)	
VI	0.433	0.391	0.391	0.485	0.539	0.645	0.615	0.573	0.620	0.679	0.644	0.686	0.596	0.378
	1.317	1.381	1.381	1.364	1.420	1.401	1.406	1.414	1.404	1.395	1.401	1.394	1.410	1.449
	1.341[c]													
VII	0.425	0.388	0.388	0.467	0.552	0.626	0.662	0.576	0.615	0.684	0.641	0.689	0.597	0.384
	1.319	1.381	1.381	1.367										
	1.343[c]													
VIII	0.432	0.400	0.394	0.506	0.531	0.647	0.613	0.564	0.633	0.630	0.602	0.700	0.582	0.375
	1.318	1.379	1.380	1.360										
	1.342[c]							(0.571)	(0.623)	(0.677)	(0.645)	(0.684)	(0.596)	

[a] See Fig. 2. Bond orders of the second phenyl ring are given in brackets.

[b] Bond lengths from Ref. [11].

[c] Obtained with Eq. (2a).

the sum of σ-bond energies and π-bonding. The latter is

$$E_{\pi b} = -(E_\pi + E_{ir} + \Sigma\,\mathrm{IP})$$

where E_π is the π-electronic energy of the molecule, E_{ir} is electrostatic repulsion energy of the core, and $\Sigma\,\mathrm{IP}$ is the sum of ionization potentials of the atoms which contribute π-electrons. The values of E_π and E_{ir} for DPPH calculated by the SCF MO LCAO method are equal to:

$$E_\pi = -2020.73\ \mathrm{eV}\,,$$
$$E_{ir} = 1482{,}84\ \mathrm{eV}\,.$$

Then, using σ-bond energies [9, 13] it is not difficult to evaluate the formation energy for the DPPH radical:

$$E = 276.82\ \mathrm{eV}\,.$$

References

1. Walter, R.: J. Amer. chem. Soc. **88**, 1930 (1966).
2. Roothaan, C. C. J.: Rev. mod. Physics **32**, 179 (1960).
3. Gubanov, V. A., Koriakov, V. I., Chirkov, A. K., Matevosian, R. O.: Zh. Struct. Khim. **11**, 1115 (1970).
4. Gubanov, V. A., Chirkov, A. K., Matevosian, R. O.: Zh. Struct. Khim. (to be published).
5. Hinze, J., Jaffé, H. H.: J. Amer. chem. Soc. **84**, 540 (1962).
6. Nishimoto, K., Mataga, N.: Z. physik. Chem. (Frankfurt) **13**, 140 (1957).
7. Pullman, B., Pullman, A.: Quantum biochemistry. New York: Interscience Publishers 1963.
8. Higasi, K., Baba, H., Rembaum, A.: Quantum organic chemistry. New York: Interscience Publishers 1965.
9. Dewar, M. J. S., Gleicher, G. J.: J. chem. Physics **44**, 759 (1966).
10. Julg, A.: Tetrahedron **19**, Suppl. 2, 25 (1963).
11. Williams, D. E.: J. Amer. chem. Soc. **88**, 23 (1966).
12. Schastnev, P. V., Zhidomirov, G. M.: Teor. i Eksper. Khim. **3**, 541 (1967).
13. Lorquet, A. J.: Theoret. chim. Acta (Berl.) **5**, 192 (1966).
14. Balaban, A. T., Frangopol, P. T., Marculescu, M.: Tetrahedron **13**, 258 (1961).
15. Turkevich, J., Selwood, P.: J. Amer. chem. Soc. **63**, 1077 (1941).
16. Matevosian, R. O.: D. dissertation, Ural Polytechnical Institute, Sverdlovsk, USSR, 1965.

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