Theoret. chim. Acta (Berl.) 15, 374—384 (1969)

Study of the Electronic Structure of Radicals by the CI Method

3. Excited States of the Benzyl Radical

YURI A. KRUGLYAK and E. V. MOZDOR

Quantum Chemistry Group, Division of Theory of Chemical Structure and Reactivity
L. V. Pisarzhevsky Institute of Physical Chemistry
Academy of Sciences of the Ukrainian SSR, Kiev, USSR

Received December 20, 1968/ August 20, 1969

There are presented the results in the π-electronic approximation for some properties of the excited doublet states of the benzyl radical obtained by the CI method on the SCF closed and open shell orbitals taking into account all singly and some doubly excited configurations. Also the first quartet and sextet states were computed by the SCF open shell theory in the one-configurational approximation. The energies and transition moments agree well with the available experimental data. The classification and the assignment of the excited terms are given. The calculated spectrum is strongly distorted when the set of all singly excited configurations is truncated. The inclusion of the doubly excited configurations leads also to a significant distortion of the spectrum changing the mutual order of the neighbouring terms in some cases. The transition from the closed shell orbitals to the open shell ones results in a considerable lowering of all terms. As in the case of the triplet molecular terms the decrease of the electronic interaction brings together the lowest excited term of the radical with its ground state term. The electronic and spin density distributions in the excited states of the benzyl radical are computed.

Die Ergebnisse von Rechnungen in der π-Elektronennäherung für einige Eigenschaften der angeregten Dublettzustände des Benzyl-Radikals, die durch das SCF-Verfahren für geschlossene und offene Schalen erzielt wurden und die alle einfach und einige zweifach angeregten Konfigurationen berücksichtigen, werden mitgeteilt. Auch die ersten Quartett- und Sextettzustände wurden in die Rechnung einbezogen. Die Energien und die Übergangsmomente stimmen gut mit den experimentellen Daten überein. Die Klassifikation und Zuordnung der angeregten Terme wird angegeben. Das berechnete Spektrum verformt sich stark, wenn man die Anzahl der einfach angeregten Konfigurationen einschränkt. Der Einschluß zweifach angeregter Konfigurationen führt ebenfalls zu einer deutlichen Verformung, wobei sich darüber hinaus auch die Reihenfolge einiger benachbarter Terme verändert. Der Übergang von Rechnungen für geschlossene Schalen zu solchen mit offenen Schalen führt zu einem beträchtlichen Absinken aller Terme. Wie im Falle der Triplett-Terme nähert sich, wenn die elektronische Wechselwirkung abnimmt, der niedrigste angeregte Term des Radikals dem Grundterm. Die Elektronen- und die Spin-Dichteverteilung wird für die angeregten Zustände berechnet.

Présentation des résultats concernant certaines propriétés des états excités doubles du radical benzyle obtenus par la méthode d'I.C. (approximation π) sur les couches complètes et ouvertes SCF en tenant compte de toutes les configurations monoexcitées et de certaines configurations diexcitées; les premiers états quartet et sextet ont aussi été étudiés dans l'approximation monoconfigurationnelle par la théorie SCF à couches ouvertes. Les énergies et les moments des transitions sont en bon accord avec les données expérimentales disponibles. Le classement et l'attribution des termes excités est fourni. Le spectre calculé est fortement distordu lorsque l'on tronque l'ensemble des configurations monoexcitées. L'introduction des configurations doublement excitées conduit aussi à des modifications significatives du spectre avec inversion possible de l'ordre mutuel des termes. Le passage des orbitales à couches fermées aux orbitales à couches ouvertes provoque un abaissement considérable de tous les termes. Comme dans le cas des termes du triplet moléculaire la diminution de l'interaction électronique rapproche du fondamental le terme excité le plus bas. Les distributions d'électron et de spin dans les états excités du radical benzyle ont aussi été calculées.

1. Introduction

Following our previous paper [1] concerned with the ground state of the benzyl radical we shall now consider its excited doublet states and the first quartet and sextet states.

At present the optical spectrum of the benzyl radical is studied experimentally fairly well. Its emission spectra is observed in the region of about 22330 cm^{-1} (2.8 eV or 4500 Å) [2–5]. In this region there was found a weak band with a maximum about 2.74 eV [6] and an oscillator strength $f \approx 0.0025$ [7]. The absorption spectrum lies in the region of about 31636 cm^{-1} (3100 Å) [6, 8–11] and it contains a band with a maximum about 3.90 eV [6] and $f \approx 0.025$ [7]. These both bands cannot be assigned to the same electronic transition. According to [5, 6, 12] they correspond to the transition from the ground state to two different excited doublet states. An analysis of the vibrational structure shows that the weak band should correspond to the transition $1^2B_2 \rightarrow {}^2A_2$ [13]. Finally, there was recently [14] reported a new transition between the ground state and the excited doublet state ${}^2B_2$ with a maximum about 4.78 eV.

The nature of the excited states of the benzyl radical was repeatedly studied theoretically. The most detailed study was done by Bingel [15]. He analyzed the benzyl spectrum by simple VB, by MO's including also the electronic interaction, and by FE methods. The two latter methods give qualitatively equal results which are, nevertheless, different of those obtained by the VB method. Bingel noted that the reason of this may be connected with the fact that he did not take into account the excited VB schemes.

Bingel's main results obtained by the MO method might be formulated as follows. Considering only the orbital transitions $3 \rightarrow 4$, $4 \rightarrow 5$, $2 \rightarrow 4$, and $4 \rightarrow 6$ Bingel obtained the excited states in a sequence[1] I^2A, II^2B, II^2A, and III^2B. The A-states correspond to the transitions $3 \rightarrow 4$ and $4 \rightarrow 5$. In the Hückel approximation they as well as both B-states indicated are degenerated. An inclusion of the electron interaction removes the degeneration [16], and the transition to the upper level thus obtained is permitted but the transition to the lower one is forbidden. Mori [17–20] has constructed a correlation diagram between the benzene and benzyl terms and has shown that the triplet benzene terms correlate with the lower benzyl terms (e.g. I^2A and II^2B) obtained by the splitting of the degenerated terms. This explains why the transition to these states is almost forbidden.

The ground state of the benzyl radical has the symmetry B. Thus, the transitions from the ground state to the excited A-states are polarized perpendicularly, and to the B-states – parallel relative to the main axes of the radical.

The transition from the Hückel orbitals to the SCF ones [21–24] changes nothing in a qualitative sense. But one must note that Mori [17–20] predicted the lowest excited state to be of the symmetry B, but not A, as in many other theoretical studies. Among the theoretical papers citied, his communication [20] contains the most detailed numerical results for the benzyl radical spectrum obtained by the CI method. As basis orbitals Mori has taken the unperturbed symmetry orbitals of benzene and of the CH_2 group.

---

[1] Here and in the following the lower right index is omitted for it is always equal to 2 for the π-states.

Hoping to obtain a more detailed interpretation of the benzyl radical spectrum we computed its excited states by the CI method using larger sets of configurations compared with the previous calculations. We constructed configurations on the SCF closed and open shell orbitals (CICS and CIOS methods). Hinchliffe *et al.* [27, 28] already published results obtained, as he wrote, by the CI method on the open shell orbitals. In our previous paper [1] we noted that the repeatition of his computation for the ground state properties of the benzyl radical did not confirm Hinchliffe's results [28]. A much greater disagreement appeared when we repeated his computations for the excited states [27].

It is appropriate to clear up the question how the results are influenced by taking into account all transitions between the one-electron orbitals of the benzyl. This will open the possibility to give a more precise interpretation of its excited states. We shall also give the results obtained considering some doubly excited configurations, and we will show how the computed spectra may change with the change of the electronic interaction and with the change of the basis used to construct the configurations.

2. Information about Computations [2]

The excited doublet states of the benzyl radical were computed by the CI method described previously [25, 26, 29, 30]. The basis SCF orbitals have been computed by the closed and open shell theory (for the CICS and CIOS methods). In the latter case the one-electron Hamiltonian for a semi-open shell [29–32] was used.

The CI was performed with five different sets of configurations II–VI. The sets II–IV were described in details previously [1]. Let us remind that the set III includes all 14 singly excited configurations of the symmetry ^2B. The set II contains those 5 of them which can interact directly with the ground state configuration. The other 9 configurations according to [26] cannot interact directly with the ground state configuration if the SCF open shell orbitals are used. In comparison with the set III, the set IV is supplemented with 10 doubly excited configurations of the symmetry ^2B (see details in [1]). The set V contains all 24 singly excited configurations of the symmetry ^2A and ^2B. Finally, the set VI includes all 10 singly excited configurations of the symmetry ^2A and 13 doubly excited configurations of the same symmetry.

The integrals γ were computed by the formulae due to Mataga-Nishimoto (MN) and Ohno. The computations were also performed with the γ's calculated by Hinchliffe *et al.* [27] using the Pariser-Parr (PP) model.

The γ's due to PP and Ohno are close to each other. The results obtained with them are also close. Thus, we shall not give the final numerical results computed with the γ's by PP. We only note that the complete repeatition of Hinchliffe's calculations also done with the γ's by PP leads to results essentially different from those published in [27].

The first quartet $1\,^4B$ and sextet $1\,^6B$ states of the benzyl radical were computed in the one-configurational approximation of the open shell theory using the one-electron Hamiltonian from [29–32].

---

[2] Necessary additional data and references see in [1].

All computations have been done on the computer M-220A of the Institute of Cybernetics of the Ukrainian Academy of Sciences (Kiev) by the programs PPP-1, PPP-2, and CI-2 described in details and listed in ALGOL 60 in the book [29].

3. Excited Doublet States

The change in the doublet state spectra of the benzyl as the CI basis becomes larger is shown in Fig. 1. The classification of the states has been done using the results obtained by the CIOS method considering all singly excited configurations (set V) and with the γ's by Ohno. It is seen from Fig. 1 that the position of some excited states is strongly changed when the complete set of all singly excited configurations is truncated. The inclusion of some doubly excited configurations also leads to a considerable change of the spectra reversing the order of the neighbouring terms in some cases. One should specially note the change of the order of two lowest excited terms. Taking into account all singly excited configurations one has a lowest excited state of the symmetry *B*. If they are supplemented with some doubly excited configurations this state becomes second, and the lowest excited term has the symmetry *A*. We note that Hinchliffe *et al.* [27] have also obtained a lowest excited term of the symmetry *A* despite the fact that these authors had not included the doubly excited configurations.

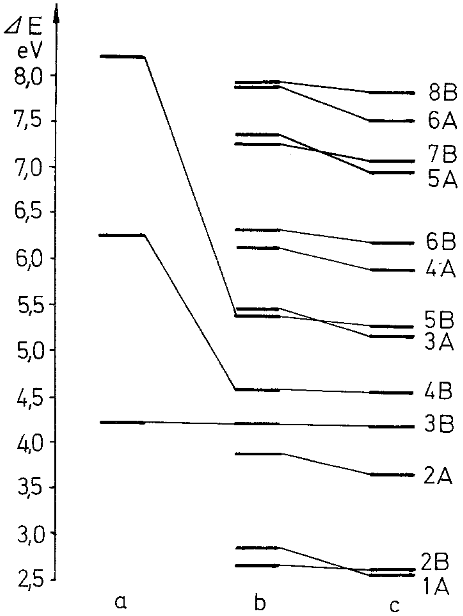

Fig. 1. The change of the doublet state spectra of the benzyl radical with an increase of the number of the basis configurations: a truncated set of the singly excited configurations (set II), b all singly excited configurations (set V), c all singly and a part of the doubly excited configurations (set IV for the *B*-states and set VI for the *A*-states), CIOS method, the γ's are those of Ohno

The change of the spectra when passing from the CIOS method to the CICS one is shown on Fig. 2 (see $b \rightarrow a$). It is seen that the use of the reminimized orbitals in the CIOS method leads to a significant lowering of all terms compared with their positions computed by the CICS method. The change of the spectra due to the use of the γ's by MN instead of those by Ohno is shown also in Fig. 2 (see $b \rightarrow c$). As in the case of the lowest triplet molecular states [33] the weakening

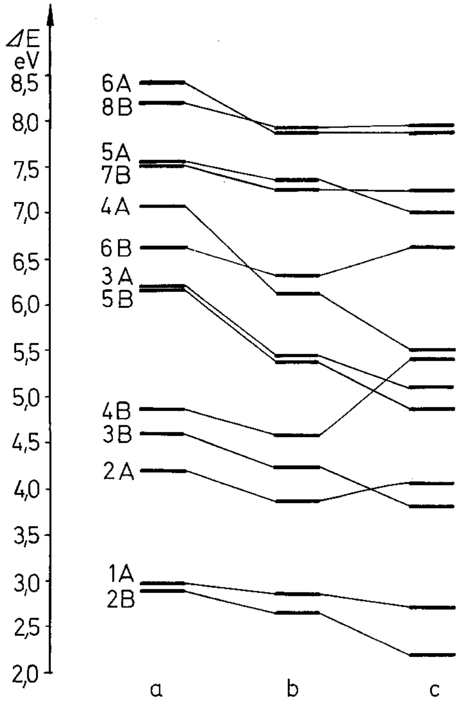

Fig. 2. The change of the doublet state spectra of the benzyl radical when passing from the CIOS method to the CICS one ($b \rightarrow a$) and caused by weakening of the electronic interaction ($b \rightarrow c$): a CICS method, γ's of Ohno; b CIOS method, γ's of Ohno; c CIOS method, γ's of MN; the set V of all singly excited configurations is used everywhere

Table 1. *The energies of the doublet states of the benzyl radical relative to its ground state energy (*CIOS *method, configurational set* V, *γ's of* Ohno*)*

Term	ΔE, eV	Term	ΔE, eV
2*B*	2.6370	5*A*	7.3613
1*A*	2.8619	6*A*	7.8781
2*A*	3.8677	8*B*	7.9361
3*B*	4.2314	9*B*	8.6058
4*B*	4.5829	7*A*	8.8332
5*B*	5.3776	10*B*	9.0393
3*A*	5.4435	8*A*	9.0394
4*A*	6.1314	11*B*	9.2570
6*B*	6.3205	9*A*	9.6822
7*B*	7.2594	10*A*	10.0738

Table 2. *The expansion coefficients of some first excited states of the benzyl radical with regard to the basis configurations (configurational set* V, *γ's of* Ohno, *most important configurations are in italics)*

Conf.	2*B*		1*A*		2*A*		3*B*		4*B*		5*B*	
	CIOS	CICS	CIOS	CICS	CIOS	CICS	CIOS	CICS	CIOS	CICS	CIOS	CICS
(−,4)	0.192	0.098	0	0	0	0	0.043	0.048	0.000	0.065	−0.018	0.174
(−,5)	0	0	*−0.559*	0.656_6	*0.550*	0.689	0	0	0	0	0	0
(−,6)	*0.535*	0.684	0	0	0	0	−0.162	0.018	*−0.466*	−0.595	0.151	0.140
(−,7)	−0.132	−0.017	0	0	0	0	−0.218	−0.451	0.098	0.063	*−0.429*	0.351
(3,44)	0	0	*0.559*	-0.657_4	*0.550*	0.622	0	0	0	0	0	0
(2,44)	*0.535*	0.608	0	0	0	0	−0.162	0.211	*0.466*	0.530	0.151	0.003
(1,44)	0.132	−0.254	0	0	0	0	0.218	0.396	0.098	−0.004	*0.429*	−0.424
(3,45)′	0.244	−0.143	0	0	0	0	*0.866*	0.709	−0.000	−0.033	−0.339	0.608
(3,46)′	0	0	*−0.340*	−0.215	*−0.440*	0.293	0	0	0	0	0	0
(3,47)′	0	0	0.182	−0.156	0.043	−0.062	0	0	0	0	0	0
(2,45)′	0	0	*0.340*	0.031	*−0.440*	0.179	0	0	0	0	0	0
(2,46)′	*−0.520*	0.171	0	0	0	0	0.239	0.248	−0.000	0.093	0.344	−0.403
(2,47)′	−0.006	−0.147	0	0	0	0	0.087	−0.060	0.064	0.078	*0.418*	0.287
(1,45)′	0	0	0.182	−0.189	−0.043	−0.034	0	0	0	0	0	0
(1,46)′	0.006	0.062	0	0	0	0	−0.087	0.083	0.064	0.034	*−0.418*	−0.131
(1,47)′	0.154	−0.084	0	0	0	0	0.159	0.111	−0.000	−0.040	−0.013	0.114
(3,45)″	−0.000	0.012	0	0	0	0	0.000	−0.050	*0.534*	−0.459	0.000	−0.003
(3,46)″	0	0	−0.194	−0.143	−0.023	−0.042	0	0	0	0	0	0
(3,47)″	0	0	0.020	0.031	0.040	0.039	0	0	0	0	0	0
(2,45)″	0	0	−0.194	−0.089	0.023	0.111	0	0	0	0	0	0
(2,46)″	0.000	0.054	0	0	0	0	−0.000	0.018	*−0.487*	0.231	−0.000	−0.034
(2,47)″	0.029	0.041	0	0	0	0	−0.043	−0.002	0.014	−0.092	−0.033	0.037
(1,45)″	0	0	−0.020	0.014	0.040	0.003	0	0	0	0	0	0
(1,46)″	0.029	0.022	0	0	0	0	−0.043	0.045	−0.014	−0.049	−0.033	−0.003
(1,47)″	−0.000	−0.015	0	0	0	0	0.000	−0.008	0.131	−0.081	−0.000	−0.001

Table 3. *The squares of the transition moments between the terms of the benzyl radical (*CIOS *method, configurational set* V, *γ's of* Ohno*)*

Term	$2B$	$1A$	$2A$	$3B$	$4B$	$5B$	$3A$	$4A$
$1B$	0	0	0.1714	0	0.2257	0	0	0
$2B$		0	0.0000	0	0.0385	0	0	0
$1A$			0.4287	0	0.0729	0	0	0
$2A$				0.0011	0	1.0448	0.0274	1.1238
$3B$					0.0765	0	0	0
$4B$						0.0070	0.1004	0.0002
$5B$							0	0
$3A$								0

of the electronic interaction leads to a lowering of the lowest radical states. For molecules this is explained by the fact that the singlet-triplet splitting is determined first of all by the electronic interaction. Then it follows that the lowest doublet states of benzyl-like radicals must also become lower for they come from the lowest triplet benzene states [17–20].

Now we shall discuss the nature of the excited doublet states. We shall rest upon the numerical results obtained by the CIOS method with the set V and with the γ's by Ohno. These computations led to a good agreement with the experimental spectra. It is now prematurely to analyze the results obtained by taking into account the doubly excited configurations for we have included only 23 of them.

The doublet state energies are given in Table 1. The expansion coefficients of some lowest excited terms with regard to all singly excited configurations are presented in Table 2. The squares of the transition moments between the ground state and some lowest excited states as well as between the excited states themselves are collected in Table 3.

The benzyl radical is an alternant hydrocarbon. Thus, all transitions between its one-electronic levels are separated into two groups. The first group will contain those transitions which have no complementary energetically alike transitions (say 1 → 7). The second group will contain complementary transitions. All of them are distributed over the irreducible representations of the C_{2v} group as follows:

A	B	
$3 \rightarrow 4 (4 \rightarrow 5)$	$3 \rightarrow 5$	$2 \rightarrow 4 (4 \rightarrow 6)$
$2 \rightarrow 5 (3 \rightarrow 6)$	$2 \rightarrow 6$	$1 \rightarrow 4 (4 \rightarrow 7)$
$1 \rightarrow 5 (3 \rightarrow 7)$	$1 \rightarrow 7$	$1 \rightarrow 6 (2 \rightarrow 7)$

As we already know each pair of the complementary transitions is degenerated if the electronic interaction is not taken into account in an explicit form. The configurations corresponding to these transitions form the appropriate linear combinations in the wave functions of the states. If the open shell orbitals which satisfy the parity theorems of the alternant hydrocarbons are used then the complementary configurations enter a given state with equal weights. This equivalence is destroyed in the CICS method where the closed shell orbitals are used (see Table 2). We note that in the frame of the CIOS method the same result is

Table 4. *The assignment of the doublet terms of the benzyl radical* (CIOS *methods, configurational set* V, *γ's of* Ohno)

Term	Assignment	Term	Assignment
$2B$	$2\to4(4\to6), 2\to6$	$1A$	$3\to4(4\to5), 2\to5(3\to6)$
$3B$	$3\to5$	$2A$	$3\to4(4\to5), 2\to5(3\to6)$
$4B$	$3\to5, 2\to6, 2\to4(4\to6)$	$3A$	$2\to5(3\to6)$
$5B$	$1\to4(4\to7), 1\to6(2\to7)$	$4A$	$1\to5(3\to7), 2\to5(3\to6)$
$6B$	$3\to5, 2\to4(4\to6)$	$5A$	$2\to5(3\to6), 3\to4(4\to5)$
$7B$	$1\to4(4\to7), 1\to6(2\to7)$	$6A$	$1\to5(3\to7), 2\to5(3\to6)$
$8B$	$2\to6, 3\to5$	$7A$	$1\to5(3\to7), 2\to5(3\to6)$

obtained when including a part of the doubly excited configurations. Nevertheless, it is believed that the inclusions of all of them will renew the equivalence of the weights.

We have found that the first excited state has the symmenty *B*. It is seen from Table 2 that this comes mainly from the transitions between the levels 2, 4, and 6. Thus, it becomes clear why Berthier [24] did not obtain this state. He has not taken into account these transitions for it has been believed that they lie energetically higher than the transitions $3\to4$ and $4\to5$ [16]. The term $2B$ corresponds to the term II*B* (see § 1) of Bingel [17]. Mori [17–20] including the transitions between orbitals 2, 4, and 6 has also obtained a lowest excited state of the symmetry *B* but incorrectly assigned it [20] to the experimentally observable so called *V*-band at 4500 Å.

It is seen from Table 2 that the term $2B$ comes from the symmetrical combination of the transition $2\to4$ and $4\to6$. Their antisymmetrical combination forms the state $4B$. According to [16] the transition to the state $4B$ must be allowed in contrast to the transition to the state $2B$. In fact, our numerical results for the transition moments (Table 3) confirm this prediction.

The recently experimentally observed transition to the state *B* with an energy of about 4.78 eV [14] corresponds well to the computed state $4B$ with an energy of 4.58 eV (Table 1). This term corresponds to Bingel's term III*B*. One may add to the interpretation due to Bingel [15] that the transition $3\to5$ which has not been taken into account by Bingel plays an important role (see Table 2).

In agreement with the results of Bingel [15] and Berthier [24] the terms $1A$ and $2A$ are mainly formed by the transitions $3\to4$ and $4\to5$. Nevertheless, the transitions $2\to5$ and $3\to6$ which have not been considered by Bingel and Berthier contribute only slightly less to the states $1A$ and $2A$. We note that in contrast to the terms $2B$ and $4B$ the antisymmetrical combination of the transition $3\to4$ and $4\to5$ corresponds to a lower term $1A$. As usually, the transition to this state is forbidden (Table 3). The computed energies of the transitions to the states $1A$ and $2A$ are equal to 2.86 and 3.87 eV (Table 1), and are in good agreement with the experimental values equal to 2.74 and 3.90 eV.

The assignment of other terms of the benzyl radical is given in Table 4. We note a good agreement for the positions of the first excited terms computed by Mori [20] and by us.

Table 5. *The electronic P_μ and spin ϱ_μ atomic densities in the excited states 1^2A, 2^2A, and 4^2B of the benzyl radical, the electronic density P_μ^v in the vacuum states*[a] (CIOS *method-upper values,* CICS *method-lower values, configurational sets* IV *and* VI), *and the unpaired electron density distribution in the lowest quartet and sextet states (γ's of* Ohno *are used everywhere)*

μ	1	2(6)	3(5)	4	7
P_μ^v	1.000	0.925	1.000	0.956	0.194
	1.124	0.817	1.004	0.746	0.487
			P_μ		
1^2A	1.029	1.022	1.005	0.987	0.928
	1.059	1.006	0.983	1.012	0.950
2^2A	1.029	0.990	0.982	1.009	1.019
	1.058	0.963	1.021	0.971	1.002
4^2B	1.019	0.999	0.998	0.980	1.006
	1.132	0.912	1.075	0.924	0.969
			ϱ_μ		
1^2A	0.015	0.255	0.275	−0.044	−0.030
	0.000	0.256	0.289	−0.081	−0.008
2^2A	0.057	0.244	0.252	0.112	−0.161
	0.025	0.258	0.233	0.117	−0.124
4^2B	0.152	0.033	0.045	0.106	0.586
	0.223	0.038	0.051	0.140	0.459
1^4B	0	0.662	0.500	0.040	0.636
1^6B	0.122	0.601	0.939	0.972	0.825

[a] See text.

In Table 5 we collected the computed values for the electronic P_μ and spin ϱ_μ density on the atoms of the benzyl radical in its excited states $1A$, $2A$, and $4B$. It is seen that the use of the CIOS method instead of the CICS one effects the electronic and spin density distribution appreciably. The electron density distribution is uniform if the CI is carried out only on all singly excited configurations.

4. The First Quartet and Sextet States

One may already find in the literature [17–21, 23, 24] about the computation of the lowest quartet state 1^4B of the benzyl radical done by the CI method [17–20, 23], in the one-configurational approximation on the closed shell orbitals [21], and by the density matrix method using the open shell theory with different MO's for each configuration [24]. These computations are interesting in connection with the position of the excited states of higher multiplicity in the benzyl spectrum. According to [21] the position of the lowest quartet term should be much closer to the ground state term than it follows from the simple Hückel scheme for alternant radicals.

According to our computations the terms 1^4B and 1^6B are 3.65 and 7.56 eV from the ground state (the γ's by Ohno were used). As it had been expected the computed energy of the transition $1^2B \rightarrow 1^4B$ equal to 3.65 eV is slightly lower than the previous estimates (3.97 [21], 3.92 [20], 3.95 [23], and 3.98 eV [24]),

Table 6. *The bond orders $P_{\mu\nu}$ in the states 1^4B and 1^6B of the benzyl radical* (*γ's of* Ohno)

State	$P_{\mu\nu}$			
	12(16)	23(56)	34(45)	17
1^4B	0.548	0.137	0.679	0.601
1^6B	0.592	0.156	0.041	0.392

as the open shell theory used by us is a better approximation for this state than those citied.

In Tables 5 and 6 we give the results of the computations for the unpaired electron density and bond orders in the states 1^4B and 1^6B. These both states have an uniform π-electronic distribution as it is in the ground state. Their open shells do not contribute to the bond orders. This is a consequence of the alternant properties of the benzyl radical. The small deviation in the electronic density distribution for the state 1^4B between the computations of Berthier [24] and ours (Table 5) is presumably explained by the fact that the MO's used by Berthier do not satisfy the alternant properties.

It is seen from Tables 5 and 6 that the quartet excitation is mainly localized on the bonds 23 and 56, and the sextet excitation captures also the bonds 34, 45, and 17.

References

1. Kruglyak, Yu. A., Mozdor, E. V.: Theoret. chim. Acta (Berl.) **15**, 365 (1969).
2. Schüler, H., Reinebeck, L., Köberle, R.: Z. Naturforsch. **7**a, 421 (1952).
3. — — Z. Naturforsch. **6**a, 160 (1954).
4. Walkers, S., Barrow, R. F.: Trans. Faraday Soc. **50**, 541 (1954).
5. Schüler, H.: Z. Naturforsch. **10**a, 459 (1955).
6. Porter, G., Strachan, E.: Spectrochim. Acta **12**, 299 (1958).
7. Leach, S.: In: Luminescence of organic and inorganic materials. N.Y.: Wiley 1962, p. 126.
8. Norman, I., Porter, G.: Nature **174**, 508 (1954).
9. Chilton, H. T. J., Porter, G.: J. physic. Chem. **63**, 904 (1959).
10. Porter, G., Land, E. J.: In: 5th international symposium on free radicals. Uppsala 1961.
11. Brocklehurst, B., Porter, G., Savadatti, M. I.: Trans. Faraday Soc. **60**, 2017 (1964).
12. Porter, G., Strachan, E.: Trans. Faraday Soc. **54**, 1595 (1958).
13. Grajcar, L., Leach, S.: C. R. Acad. Sci. **252**, 1014 (1961).
14. Porter, G., Savadatti, M. I.: Spectrochim. Acta **22**, 803 (1966).
15. Bingel, W.: Z. Naturforsch. **10**a, 462 (1955).
16. Dewar, M. J. S., Longuet-Higgins, H. C.: Proc. physic. Soc. A **67**, 795 (1954).
17. Mori, Y.: J. chem. Physics **24**, 1253 (1956).
18. Komatsu, C., Mori, Y., Tanaka, I.: J. chem. physic. Soc. Japan **77**, 643 (1956).
19. Mori, Y.: Bull. chem. Soc. Japan **34**, 1031 (1961).
20. — Bull. chem. Soc. Japan **34**, 1035 (1961).
21. Longuet-Higgins, H. C., Pople, J. A.: Proc. physic. Soc. A **68**, 591 (1955).
22. Brion, H., Lefebvre, R., Moser, C.: J. Chim. physique **54**, 363 (1957).
23. Bertheuil, C.: C. R. Acad. Sci. **256**, 5097 (1963).
24. Berthier, G.: In: Molecular orbitals in chemistry, physics, and biology, p. 57. N. Y.: Academic Press 1964.
25. Kruglyak, Yu. A., Kuprievich, V. A., Mozdor, E. V.: In: Structure of molecules and quantum chemistry, ed. A. I. Brodsky, Kiev: Publishing House "Naukova Dumka" 1970.

26. Mozdor, E. V., Kruglyak, Yu. A., Kuprievich, V. A.: Theoret. i Eksperim Khimiya (U.S.S.R.) **5**, 723 (1969).
27. Hinchliffe, A., Stainbank, R. E., Ali, M. A.: Theoret. chim. Acta (Berl.) **5**, 95 (1966).
28. — Theoret. chim. Acta (Berl.) **5**, 208 (1966).
29. Kruglyak, Yu. A., Dyadyusha, G. G., Kuprievich, V. A., Podolskaya, L. M., Kagan, G. I.: Methods of computation of electronic structure and spectra of molecules, ch. 3, p. 205 (in Russian). Kiev: Publishing House "Naukova Dumka" 1969.
30. — On calculation of the electronic structure of conjugated molecules and radicals by self-consistent field and configuration interaction methods. In: Kayushin, L. P., Pulatova, M. K., L'vov, K. M.: Study of paramagnetic centers of irradiated proteins (in Russian). Moscow: Publishing House "Nauka" 1969.
31. Kuprievich, V. A.: Intern. J. quant. Chem. **1**, 561 (1967).
32. Kruglyak, Yu. A., Dyadyusha, G. G.: Theoret. chim. Acta (Berl.) **12**, 18 (1968).
33. Danilov, V. I., Kruglyak, Yu. A., Kuprievich, V. A., Ogloblin, V. V.: Theoret. chim. Acta (Berl.) **14**, 242 (1969).

Assoc. Prof. Yuri A. Kruglyak
Quantum Chemistry Group
Institute of Physical Chemistry
Academy of Sciences of the Ukrainian SSR
Prospect of Science 97, Kiev-28, USSR