# Physical Chemistry

## Color centers in poly(arylenesulfophthalides) and the ground state of Müller's hydrocarbon molecule

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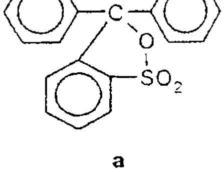
Published data on the properties of Müller's hydrocarbon are analyzed. The total energies of several hydrocarbon biradicals with *p*-phenylene bridges, including Thiele's, Chichibabin's, and Müller's hydrocarbons in the singlet and triplet states were calculated by the AM1 and PM3 semiempirical quantum-chemical methods. Contrary to popular opinion, our calculations revealed that the Müller's hydrocarbon molecule has a triplet rather than singlet ground state. The results obtained make it possible to explain the fact that quinoid color centers do not form in the course of reduction of poly(terphenylsulfophthalide). The calculated parameters of electronic spectra for singlet states of some related biradicals are reported.

**Key words:** biradicals, Müller's hydrocarbon, Chichibabin's hydrocarbon, Thiele's hydrocarbon, quantum-chemical calculations, semiempirical AM1 and PM3 methods, electronic spectra, color centers, poly(arylenesulfophthalides).

We faced the problem of the ground state of Müller's hydrocarbon molecule in studies of the chemical properties of poly(arylenesulfophthalides). Previously,[1,2] we have found that triarylmethyl radicals are generated in the reductive reactions of diphenylsulfophthalide (**a**) and poly(terphenylsulfophthalide) (**b**). The reduction of poly(arylenesulfophthalides) (**c** and **d**) results not only in radicals, but also in blue color centers, which were attributed to quinoid structures similar to Chichibabin's hydrocarbon.[1,2] The assumption that the Müller hydrocarbon molecule should be regarded as having the triplet ground state makes it possible to rationalize the absence of quinoid color centers from polymer **b**. On the other hand, this assumption contradicts a popular opinion that this biradical has the singlet ground state. In this work, a critical analysis of published data on the properties of Müller's hydrocarbon is given and the results of quantum-chemical calculations of selected parameters of this molecule and a number of related structures are reported.



**a**

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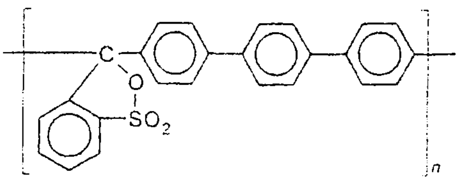

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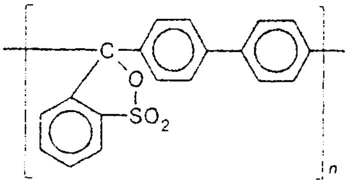
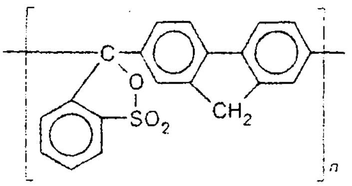
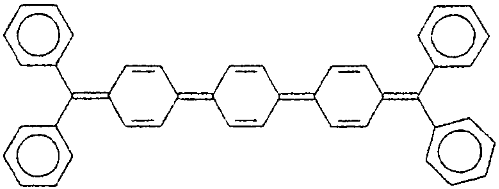


**c**

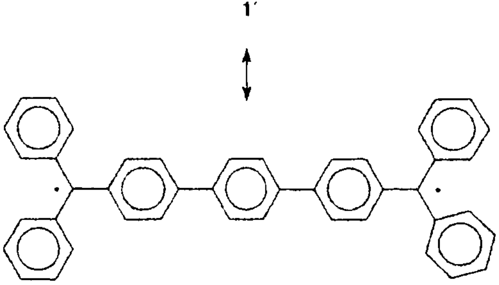


**d**

Müller's hydrocarbon (**1**) was first synthesized in 1941.[3] As for other biradicals, two states are usually considered for this hydrocarbon, a singlet state with a quinoid structure (**1′**) and a triplet state with two unpaired electrons (structure **1″**). The two states should be in equilibrium.



**1′**



**1″**

The EPR signal of **1** with the zero-field splitting (ZFS) parameters $D = 38$ G and $E \leq 2$ G was attributed[4] to the triplet state of the molecule. Studies of the temperature dependence of the signal amplitude made it possible to conclude[4] that molecule **1** has a singlet ground state with an energy ~1 kcal $mol^{-1}$ lower than that of the triplet state. Since this was consistent with the results of earlier theoretical studies,[5–8] the singlet state came to be regarded as the ground state of the Müller hydrocarbon molecule.[9–11]

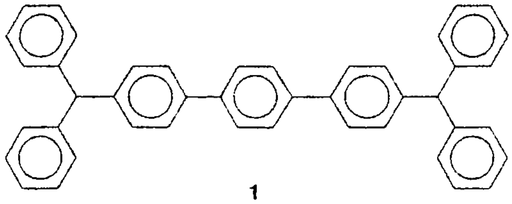
On the other hand, comparison of the data on the properties of the Müller and Chichibabin hydrocarbons reveals at least two reasons which cast some doubt on the validity of the conclusions drawn previously.[4] (After solving the famous McConnel biradical paradox,[12] the studies of Chichibabin's hydrocarbon are still far from being completed.[13–15]) For instance, it was concluded[14] that previous attribution[16] of the EPR signal of seemingly triplet Chichibabin's hydrocarbon molecules should be revised since the signal is most likely due to the radical pairs rather than to the triplet molecules. It is also believed[14] that in the latter case the ZFS parameters should be much smaller than the experimental values,[16] which, in turn, should hamper the observation of the signal of the triplet Chichibabin's hydrocarbon molecules against the background of the signal of monoradical species. Moreover,[14] that is why no EPR signals corresponding to the triplet state were observed in studies[13] of single crystals of Chichibabin's hydrocarbon.

Since the distance between the radical centers in molecule **1** is ~1.5 times longer than that in the Chichibabin hydrocarbon molecule, one should expect that, in the dipole-dipole approximation, the ZFS parameters for the former molecule are 2.25 times smaller than those for the latter. Taking into account the conclusions drawn earlier,[14] it is highly probable that the EPR signal observed previously[4] was due to intermolecular radical pairs rather than to triplet molecules **1**. As a consequence, the conclusion that the Müller hydrocarbon molecule has a singlet ground state seems to be ambiguous and calls for further investigation.

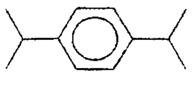
The absence of both deep color and strong absorption bands from the electronic spectra of Müller's hydrocarbon in the visible region (see experimental studies[3,4]) is the second point which casts doubt on the singlet ground state of molecule **1**. For instance, the singlet quinoid structure of Chichibabin's hydrocarbon is characterized by a deep blue color in solution and by two intense absorption bands at 570 and 310 nm ($\varepsilon = 10^5$ and $1.4 \cdot 10^4$ L mol $cm^{-1}$, respectively) in the electronic spectrum.[13] It was reasonable to assume that even more intense absorption bands in the electronic spectrum, shifted toward the long-wavelength region, and a deeper color should correspond to the more developed singlet quinoid structure of molecule **1**, if it exists. However, no indications of deep color of Müller's hydrocarbon (including low-temperature studies) have been reported.[3,4]

The observed[3] changes in color can easily be explained by allowed and forbidden electronic transitions in monomeric radicals, which are present in the system in a considerable amount. Deeper coloration on heating[3] is due to dissociation of dimeric and polymeric radical species and also corresponds to the monoradical attribution of color centers. On the other hand, the color due to the presence of the singlet quinoid form of Müller's hydrocarbon would be deeper with decreasing temperature owing to increasing the concentration of this form.

Based on the aforesaid, one can conclude that further investigation of the problem by semiempirical quantum-chemical methods is required. In particular, the AM1 and PM3 methods are widely and successfully used for the determination of the ground state of bi- and polyradicals (see, *e.g.*, Refs. 17—19 and references cited therein) by comparing the calculated total energies for different types of states. Therefore, to determine the multiplicity of the ground state of the Müller hydrocarbon molecule, we performed PM3 and AM1 calculations of molecule **1** and related structures **2—8** including Thiele's (**3**) and Chichibabin's (**5**) hydrocarbons and compared (i) the total energies of the singlet and triplet states of these structures, (ii) the calculated and experimental[13] structural parameters of molecules **3** and **5**, and (iii) the calculated and experimental[13,25] electronic spectra of the singlet states of biradicals **1—3** and **5**.



**1**



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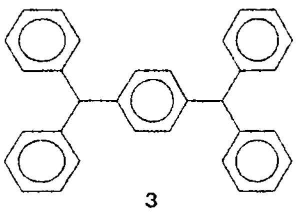
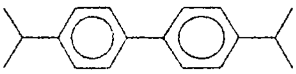


**3**



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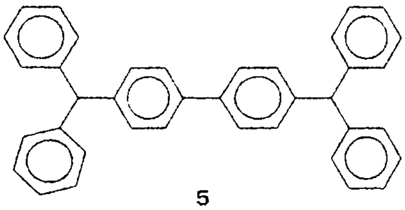
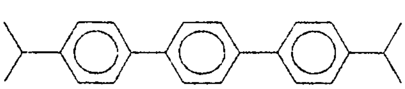


**5**



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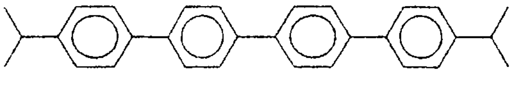

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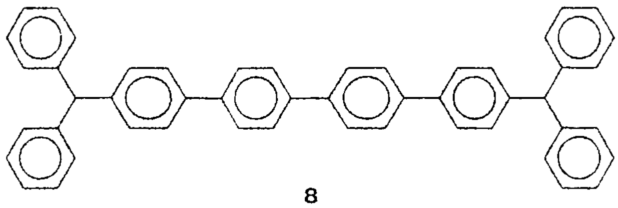

**8**

Apart from the above-mentioned systematic applications of the extended Hückel theory,[5–7] only a few quantum-chemical calculations of selected parameters of particular structures have been reported so far. These are MNDO calculations of molecule **3** [20] and PPP calculations of the electronic spectrum of compound **5** performed with consideration of the configuration interaction.[21] Recently,[15] selected parameters of molecule **5** have also been found from extended Hückel calculations of the structure of hydrocarbon biradicals. Some related structures were analyzed[22] using the Heisenberg Hamiltonian and it was concluded that the contribution of the biradical structure increases as the number of benzene rings in the bridge between the radical centers increases. Simultaneously, it was confirmed that molecule **1** and related molecules should be regarded as having the singlet ground state.

## Calculation Procedure

Calculations were performed using the HyperChem 5.0 program package and procedures proposed for biradicals.[17,18] The initial geometries of structures **1—8** were determined by the molecular mechanics (MM+) method following a previously described calculation procedure.[18] Then, the PM3 and AM1 calculations with full geometry optimization for all structures were carried out in the framework of the restricted (RHF, for the singlet states) and unrestricted Hartree—Fock (UHF, for the triplet states) schemes. The optimized structures of the biradicals thus obtained were then used for the RHF calculations of the total energies of the singlet and triplet states of the biradicals, performed with consideration of the configuration interaction between the five highest occupied and five lowest unoccupied molecular orbitals (a 5×5 CI).

## Results and Discussion

The calculated singlet-triplet energy differences for structures **1—8** are listed in Table 1. For comparison, we also report here the results of extended Hückel[6] and perturbation theory calculations.[8] It should be noted that the structures studied in this work were chosen in accordance with the known recommendations.[6]

The presence of one phenyl ring in the *p*-phenylene bridge makes the singlet state of compound **3** and its hydrogen-substituted analog very energetically favorable. This state corresponds to the canonical quinoid structure, which is so energetically favorable that no monoradical species are formed in the synthesis of **3**.[23]

According to calculations, the triplet state of structure **5** appeared to be the most stable. This is contrary to

**Table 1.** The singlet-triplet energy differences ($\Delta E$) for hydrocarbon biradicals **1**—**8** calculated by different methods

| Structure | $\Delta E$/eV | | | |
|---|---|---|---|---|
| | EHT[a] | PT[b] | PM3[c] | AM1[c] |
| **1** | −0.056 | −0.0074 | 0.79 | 1.03 |
| **2** | −0.46 | | −0.61 | −0.60 |
| **3** | −0.23 | | −0.80 | −0.59 |
| **4** | −0.20 | | 0.08 | 0.12 |
| **5** | −0.11 | −0.01 | 0.10 | 0.16 |
| **6** | −0.096 | | 0.67 | 0.65 |
| **7** | −0.052 | | 1.38 | 1.33 |
| **8** | −0.030 | −0.0024 | 1.56 | 1.79 |

[a] Data taken from Ref. 6.

[b] Perturbation theory calculations.[8]

[c] This work.

**Table 2.** Structural parameters of the Thiele hydrocarbon molecule

| Parameter | Experimental[a] | Calculated[b] | |
|---|---|---|---|
| | | PM3 | AM1 |
| Bond | $d$/Å | | |
| C(1)—C(2) | 1.346 | 1.342 | 1.347 |
| C(2)—C(3) | 1.449 | 1.458 | 1.457 |
| C(3)—C(4) | 1.381 | 1.356 | 1.359 |
| C(4)—C(5) | 1.479 | 1.473 | 1.469 |
| $C_{Ar}$—$C_{Ar}$ | 1.389 | 1.389 | 1.398 |
| Bond angle | $\omega$/deg | | |
| C(1)—C(2)—C(3) | 122.88 | 121.92 | 122.17 |
| C(2)—C(3)—C(1′) | 114.24 | 116.15 | 115.66 |
| C(6)—C(5)—C(10) | 117.10 | 119.83 | 119.37 |
| C(5)—C(6)—C(7) | 121.38 | 119.91 | 120.18 |
| C(6)—C(7)—C(8) | 120.27 | 120.20 | 120.21 |
| C(7)—C(8)—C(9) | 119.60 | 119.98 | 119.85 |
| Torsion angle | $\tau$/deg | | |
| C(1′)—C(3)—C(4)—C(5) | 13.87 | 2.61 | 2.65 |
| C(3)—C(4)—C(5)—C(6) | 43.37 | 71.02 | 70.59 |

[a] Data of X-ray study.[13]

[b] This work.

facts, since compound **5** is known to exist both in solution and in the solid state at ambient temperatures as a colored singlet quinoid form with some fraction of monoradical species (see Ref. 13 and references cited therein). Hence, the semiempirical methods employed here are not quite adequate for the description of the hydrocarbon biradicals under study. Strictly speaking, the results of calculations should be compared with gas-phase data on compound **5**, which, as far as we know, are unavailable. Most likely, the singlet-triplet energy gap for molecule **5** is not too wide, which is probably the main reason for errors and contradictions in the concepts of Chichibabin's hydrocarbon.[13,14] For structure **1**, the triplet state appears to be so energetically more favorable than the singlet state (by ~1 eV) that the formation of singlet quinoid structure is hardly probable even taking into account incomplete adequacy of the computational methods used.

Let us compare the calculated structural parameters of singlet molecules **3** and **5** with the results of X-ray diffraction study[13] (Tables 2 and 3, Fig. 1). For compound **3**, the calculated bond lengths and most of the angle values are close to those determined by X-ray

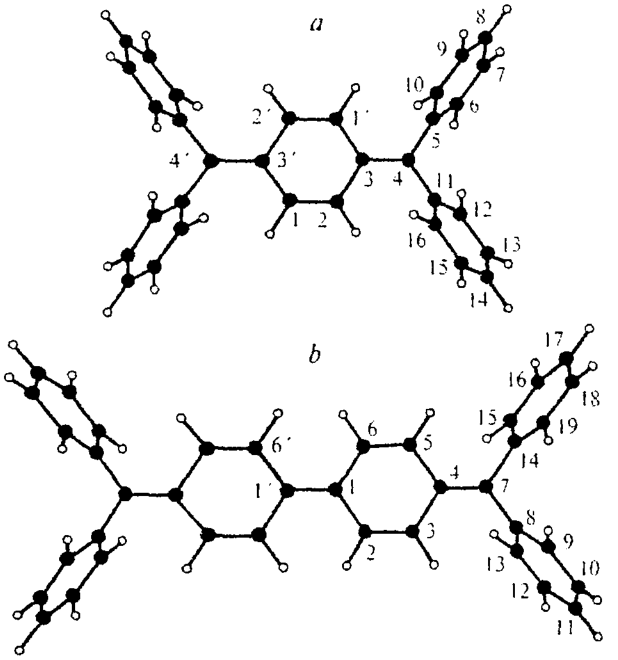

**Fig. 1.** The numbering of atoms in the molecules of Thiele's (*a*) and Chichibabin's (*b*) hydrocarbons.

**Table 3.** Structural parameters of the Chichibabin hydrocarbon molecule

| Parameter | Experimental[a] | Calculated[b] | |
|---|---|---|---|
| | | PM3 | AM1 |
| Bond | $d$/Å | | |
| C(1)—C(1′) | 1.448 | 1.371 | 1.374 |
| C(1)—C(2) | 1.420 | 1.452 | 1.452 |
| C(2)—C(3) | 1.372 | 1.345 | 1.350 |
| C(3)—C(4) | 1.429 | 1.456 | 1.453 |
| C(4)—C(5) | 1.424 | 1.456 | 1.453 |
| C(5)—C(6) | 1.371 | 1.344 | 1.350 |
| C(1)—C(6) | 1.420 | 1.452 | 1.452 |
| C(4)—C(7) | 1.415 | 1.359 | 1.363 |
| $C_{Ar}$—$C_{Ar}$ | 1.391 | 1.393 | 1.396 |
| Bond angle | $\omega$/deg | | |
| C(2)—C(3)—C(4) | 121.73 | 121.73 | 122.28 |
| C(2)—C(1)—C(6) | 115.94 | 116.26 | 114.98 |
| C(3)—C(4)—C(5) | 115.69 | 116.21 | 115.20 |
| Torsion angle | $\tau$/deg | | |
| C(6′)—C(1′)—C(1)—C(6) | 0.58 | 6.75 | 11.76 |
| C(5)—C(4)—C(7)—C(14) | 22.70 | 8.39 | 5.79 |
| C(4)—C(7)—C(14)—C(15) | 36.91 | 64.92 | 59.77 |

[a] Data of X-ray study.[13]

[b] This work.

diffraction analysis. The largest differences were found for the length of the C(3)—C(4) bond between the bridging phenyl ring and the quaternary C atom (0.025 Å) and for the torsion angles of rotation of the outermost phenyl rings with respect to the bridge plane (C(3)—C(4)—C(5)—C(6), ~28°). For structure **5**, the length of the C(1)—C(1´) bond between the phenyl rings of the biphenyl bridge and that of the C(4)—C(7) bond between the bridging phenyl ring and the quaternary C atom, obtained from PM3 calculations, are shorter than the experimental values by 0.077 and 0.056 Å, respectively. The angle of rotation of the outermost phenyl rings with respect to the bridge plane in the single crystal of **5** is also 28° smaller than that in the optimized structure of the Chichibabin hydrocarbon molecule. Rather large differences between the calculated and experimental values of some parameters are likely due to the distortions of the equilibrium structures of hydrocarbons in crystals owing to intermolecular interactions and to incomplete adequacy of computational methods employed in this work.

According to PM3 calculations, the distance $R$ between the radical centers of triplet molecule **1** is 14.28 Å. In the point dipole approximation, which can well be applied with such a long $R$, the ZFS parameter $D$ is expressed through the $g$-factor of the free electron and the Bohr magneton $\mu_B$, $D = 3g\mu_B/2R^3$, from where $D$ = 9.6 G, which is nearly 4 times smaller than the experimental value.[4] In our opinion, this estimate also contradicts the attribution of the experimental EPR spectrum[4] to the triplet state of the Müller hydrocarbon molecule.

The results of PM3 calculations of the parameters of the electronic spectra for the singlet states of hydrocarbons **1**—**3** and **5** are listed in Table 4. For each structure, we calculated the parameters of the first eight transitions only. It should be noted that this computational method has no parametrization for correct reproduction of spectral data. Hence, quantitative agreement between the calculated energies and transition intensities and the corresponding experimental values can hardly be obtained. For instance, the difference between the calculated and experimental energies of the absorption band corresponding to the HOMO—LUMO transition in molecule **5** is nearly 90 nm. However, even these rough calculations seem to be more realistic and informative than, *e.g.*, PPP calculations[21] of the electronic spectrum of compound **5** performed assuming a planar molecular structure, which is explicitly contrary to facts.

**Table 4.** Parameters of electronic spectra of structures **1**—**3** and **5** in the singlet state obtained from PM3 calculations

| Transition number | **2** | **3** | **5** | **1** |
|---|---|---|---|---|
| 1 | 852[a] | 663 | 1038 | 1431 |
| | 1[b] | 1 | 1 | 1 |
| | 0.0[c] | 0.0 | 0.0 | 0.0 |
| 2 | 404 | 343 | 474 | 632 |
| | 1 | 0 | 0 | 1 |
| | 0.0 | 1.4317 | 2.2469 | 0.0 |
| 3 | 397 | 274 | 429 | 567 |
| | 1 | 1 | 1 | 0 |
| | 0.0 | 0.0 | 0.0 | 2.8938 |
| 4 | 312 | 273 | 287 | 330 |
| | 0 | 1 | 0 | 1 |
| | 1.2187 | 0.0 | 0.0 | 0.0 |
| 5 | 288 | 252 | 286 | 329 |
| | 0 | 0 | 1 | 0 |
| | 0.0 | 0.0045 | 0.0 | 0.0 |
| 6 | 265 | 251 | 285 | 318 |
| | 1 | 0 | 0 | 0 |
| | 0.0 | 0.2845 | 0.0 | 0.0001 |
| 7 | 260 | 242 | 270 | 292 |
| | 1 | 1 | 1 | 1 |
| | 0.0 | 0.0 | 0.0 | 0.0 |
| 8 | 259 | 235 | 261 | 245 |
| | 0 | 0 | 1 | 0 |
| | 0 | 0 | 0 | 0.0320 |

*Note*. The parameters of the 0—0 transitions are listed.

[a] Transition energy/nm.

[b] Multiplicity: singlet (0), triplet (1).

[c] Oscillator strength.

Analysis of the spectral parameters listed in Table 4 makes it possible to draw two important conclusions. First, a spin-forbidden triplet transition in the near IR region can occur in the hydrocarbons under study (taking into account the difference between calculated and experimental energies, for structure **5** this transition should be in the region ~1500 nm). Provided that the corresponding compounds could be synthesized, one can expect phosphorescence upon photoexcitation, as well as chemiluminescence in the IR spectral region. On the other hand, the probability of radiationless de-excitation increases substantially owing to the low transition energy.[24] Second, very intense singlet HOMO—LUMO transitions in the UV (for compounds **2** and **3**) and visible (for **5** and **1**) spectral regions are characteristic of all the hydrocarbons. Compared to molecule **5**, the transition intensity for **1** should be even higher and its energy should be shifted toward the long-wavelength region. For structures **2**, **3**, and **5**, these transitions have been found experimentally.[13,25] However, neither intense color nor strong absorption bands have been found for **1** even at low temperatures (see above). We believe that this points to the fact that the Müller hydrocarbon molecule should be regarded as having the triplet rather than singlet ground state.

Thus, comparison of the energy parameters of the electronic spectrum of compound **1** and related structures, obtained from semiempirical quantum-chemical calculations, suggests that the Müller hydrocarbon molecule has the triplet ground state. Experimental observation of this state is likely hampered both by small ZFS parameters $D$ and $E$ and by enhanced reactivity of **1** in the triplet state. Nevertheless, it is experimental methods that will play a decisive role in solving the problem of the ground state of Müller's hydrocarbon molecule.

Because of enhanced reactivity, triplet hydrocarbon biradicals can form dimeric and polymeric structures with relative ease. Probably, the synthesis of polymers of types **b—d**, containing biradical fragments structurally similar to the hydrocarbon biradicals under study in the polymer chain, which hampers chemical interactions between them, will allow more in-depth investigations of the properties of such species. In particular, it is of interest whether or not the EPR signal from the triplet fragments structurally similar to Chichibabin's hydrocarbon can be observed in polymers of the types **c** and **d**. Taking into account our viewpoint of the problem of the ground state of the Müller hydrocarbon molecule, it is also of interest to establish whether or not (i) a high density of the unpaired electrons can be concentrated in polymers of type **b** and (ii) the in-chain interaction between the unpaired electrons will be cooperative.

The quinoid attribution of color centers in polymers of types **c** and **d** implies a concerted dissociative reduction of sulfophthalide rings at adjacent quaternary C atoms of the main chains of the polymers. This can be considered here as a pronounced neighbor effect, which is well known in polymer chemistry.[26] Studies on the reactions of sulfophthalide-containing compounds with lithium metal in DMSO also confirmed that radicals and color centers can be generated in the electron transfer reactions.[2] Most likely, the presence of quinoid structures similar to Chichibabin's hydrocarbon in the main chain is an inherent characteristic of this type of polymers and is not necessarily due to electron transfer reactions. For instance, recently[27] it was suggested that quinoid structures can be generated in the thermolysis of poly(triphenylcarbinol), which is a derivative of polymer **c**.

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