

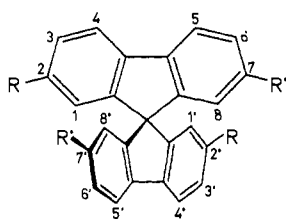
## Spin Localization in the Spirobifluorene Radical Anion

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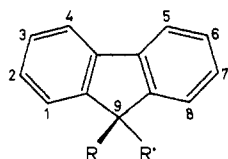
Contribution from the Physikalisch-Chemisches Institut der Universität, 4056 Basel, Switzerland. Received August 22, 1973

**Abstract:** Electron spin resonance studies were performed on the radical anion of spirobifluorene. Spectra characteristic of spin delocalization over the two mutually perpendicular fluorene moieties are observed, as well as those indicating spin localization on one moiety. Prolonged reduction time and nonpolar solvents favor the localization which is thought to be promoted by the association of the radical anion with its counterion.

The esr spectrum of the radical anion of bis(*o,o'*-biphenylene)methane or spirobifluorene (**1**) was reported several years ago,<sup>2</sup> along with the suggestion that spin delocalization occurs over the two mutually perpendicular  $\pi$  systems. However, no analysis of the hyperfine structure was given. Recently, esr studies were carried out on the radical anion of spiro[5.5]-undeca-1,4,6,9-tetraene-3,8-dione<sup>3</sup> in which the spin population is essentially localized on one dienone moiety. This observation prompted us to reinvestigate the esr spectrum of **1**<sup>•-</sup>. In addition, we studied the radical anions of 2,2'-di-*n*-propyl-7,7'-diethylspirobifluorene (**2**), fluorene (**3**), and several substituted fluorenes. Esr data for **3**<sup>•-</sup> and some of its derivatives (**4**<sup>•-</sup>, **5**<sup>•-</sup>, and **6**<sup>•-</sup>) were reported previously.<sup>4,5</sup>



1: R = R' = H  
2: R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> R' = CH<sub>2</sub>CH<sub>3</sub>



3: R = R' = H  
4: R = CH<sub>3</sub> R' = H  
5: R = R' = CH<sub>3</sub>  
6: R = R =   
7: R-R' = H<sub>2</sub>C-CH<sub>2</sub>  
8: R = CH<sub>2</sub>CH<sub>3</sub> R' = H  
9: R = R' = H

## Experimental Section

The spirobifluorenes **1** and **2** were kindly provided by Professor V. Prelog, Eidg. Technische Hochschule, Zürich.

The 9,9-diphenylfluorene (**6**) was a gift of Professor E. G. Janzen, University of Georgia, Athens, whereas Dr. A. Braun, CIBA-GEIGY, Basel, generously supplied the parent compound (**3**) and its derivatives **4**, **5**, and **7**.

The radical anions **1**<sup>•-</sup> to **6**<sup>•-</sup> were produced by reaction of the respective neutral molecules with potassium or sodium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), or 2-methyltetrahydrofuran (MTHF). The spirobifluorene radical anion (**1**<sup>•-</sup>) was also generated by electrolysis of **1** in *N,N*-dimethylformamide (DMF) with tetraethylammonium perchlorate as the supporting salt.

(1) Address correspondence to this author.

(2) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **38**, 2028 (1963).

(3) F. Gerson, R. Gleiter, G. Moshuk, and A. S. Dreiding, *J. Amer. Chem. Soc.*, **94**, 2919 (1972).

(4) D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 887 (1969), and references therein.

(5) E. G. Janzen, W. B. Harrison, and J. B. Pickett, *J. Organometal. Chem.*, **16**, 48 (1969).

Because of the instability of the radical anions their esr investigations had to be conducted at temperatures below  $-20^{\circ}$ .

Upon alkali metal reduction of spiro[cyclopropanefluorene] (**7**) only a secondary radical anion could be detected which was identified by esr spectroscopy as that of 9-ethylfluorene (**8**) (*vide infra*).

## Results and Discussion

Figure 1 shows the esr spectra of **1**<sup>•-</sup> taken in THF at  $-60^{\circ}$ , the time of exposure (*t*) to a potassium mirror increasing from  $\sim 1$  (*t*<sub>1</sub>) to  $\sim 30$  min (*t*<sub>6</sub>). Short contact with the alkali metal (*t*<sub>1</sub>) results in the first spectrum (a) the hyperfine structure of which is due to *four* sets of *four* equivalent protons. Upon prolonged reduction (*t*<sub>2</sub> and *t*<sub>3</sub>) every second line becomes gradually weaker until the spectrum b is obtained (*t*<sub>4</sub>). Further reaction (*t*<sub>5</sub>) gives rise to slight changes in the hyperfine splittings which finally (*t*<sub>6</sub>) lead to the spectrum c. Spectra b and c are analyzed in terms of *four pairs* of equivalent protons, the coupling constants now being *twice* as large as those for a. At all reduction stages, raising of the temperature causes a sharp decrease in spectral intensity without markedly altering the hyperfine structure.

When another solvent and/or reducing agent is used, only initial or final stages of the sequence a  $\rightarrow$  b  $\rightarrow$  c are observed. Table I summarizes the results. Two

Table I. ESR Spectra of **1**<sup>•-</sup> Obtained under Various Conditions<sup>a</sup>

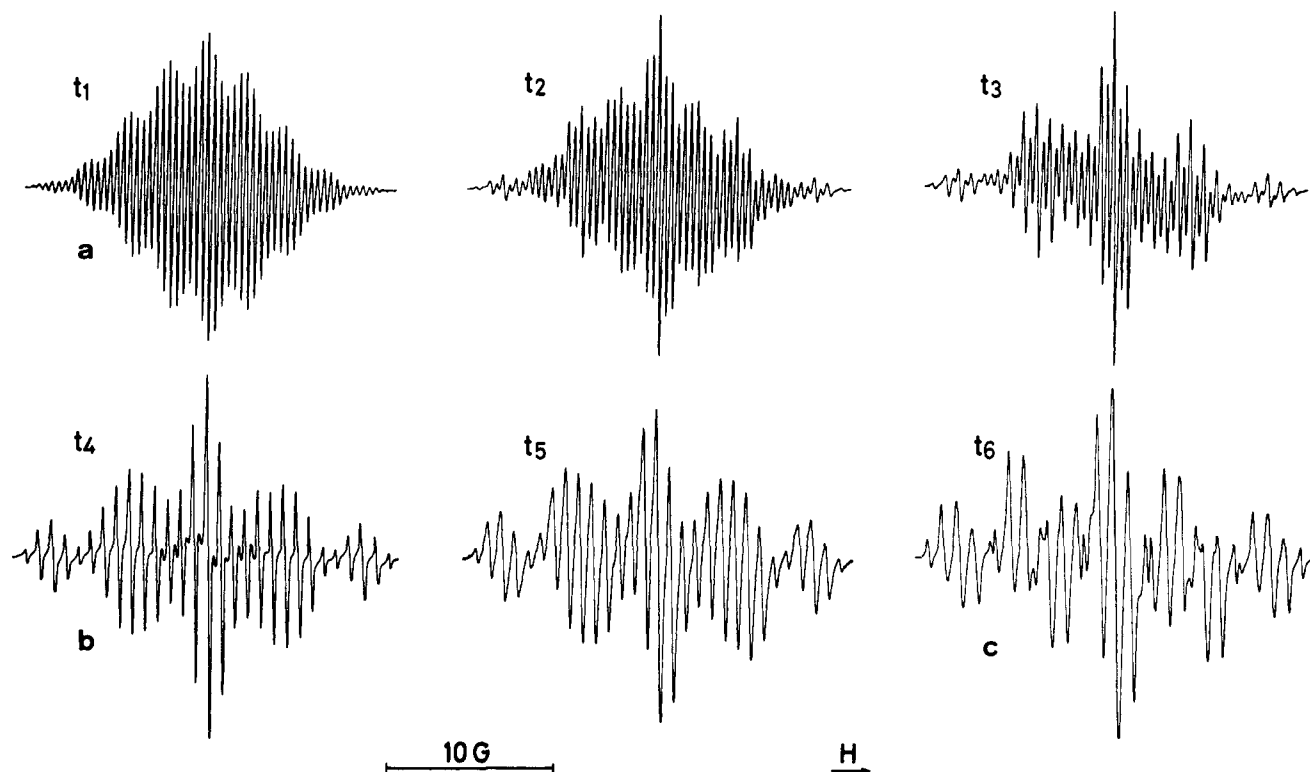
Red. agent (counterion)	Solvent			
	DMF	DME	THF	MTHF
Potassium (K <sup>+</sup> )		a $\rightarrow$ b	a $\rightarrow$ b $\rightarrow$ c	c
Sodium (Na <sup>+</sup> )		a $\rightarrow$ b	a $\rightarrow$ b	b $\rightarrow$ c
Electrolysis (Et <sub>4</sub> N <sup>+</sup> )	a			

<sup>a</sup> Classification according to Figure 1.

border cases are noteworthy. Reaction of **1** with potassium in MTHF immediately yields spectrum c, whereas in the course of electrolysis in DMF only spectrum a is obtained, even after several hours of continuous reduction.

The behavior of 2,2'-di-*n*-propyl-7,7'-diethylspirobifluorene (**2**) upon reduction closely parallels that of the parent compound **1** under the same experimental conditions. Thus the spectrum of **2**<sup>•-</sup> corresponding to a is dominated by a hyperfine interaction with 12 protons. On the other hand, in the spectra analogous to b or c (they cannot be distinguished for **2**<sup>•-</sup>) the major splitting stems from only *six* protons, albeit with coupling constants *twice* as large.

Table II lists the esr data for **1**<sup>•-</sup> and **2**<sup>•-</sup>. The assignment is based on comparison with the proton coupling constants observed for the radical anions of



**Figure 1.** ESR spectra of spirobifluorene radical anion ( $1\cdot^-$ ): solvent, THF; counterion,  $K^+$ ; temperature,  $-60^\circ$ ;  $t_1 < t_2 < t_3 < t_4 < t_5 < t_6$  = periods of exposure to a potassium mirror.

**Table II.** Proton Coupling Constants (in G)<sup>a</sup> for the Radical Anions of the Spirobifluorenes **1** and **2**, and of the Fluorenes **3**, **4**, **5**, and **6**<sup>e</sup>

Radical anion	Position				
	1,8 or 3,6	2,7	3,6 or 1,8	4,5	9
<b>1</b> · <sup>-</sup> { a	0.39 (4 H)	2.66 (4 H)	0.42 (4 H)	1.93 (4 H)	
{ b	0.78 (2 H)	5.33 (2 H)	0.80 (2 H)	3.82 (2 H)	
{ c	0.89 (2 H)	5.22 (2 H)	0.91 (2 H)	3.98 (2 H)	
<b>2</b> · <sup>-</sup> { (a) <sup>b</sup>	~0.4 (4 H)	2.1 (8 H) <sup>c</sup>	~0.4 (4 H)	1.7 (4 H)	
{ (b, c) <sup>b</sup>	0.95 (2 H)	4.2 (4 H) <sup>c</sup>	0.95 (2 H)	3.4 (2 H)	
<b>3</b> · <sup>-</sup>	0.89 (2 H)	5.12 (2 H)	1.21 (2 H)	3.85 (2 H) <sup>d</sup>	4.21 (2 H) <sup>d</sup>
<b>4</b> · <sup>-</sup>	0.89 (2 H)	5.17 (2 H)	1.00 (2 H)	4.09 (2 H)	4.16 (1 H)
<b>5</b> · <sup>-</sup>	0.91 (2 H)	5.22 (2 H)	0.91 (2 H)	4.06 (2 H)	
<b>6</b> · <sup>-</sup>	0.62 (2 H)	5.20 (2 H)	0.76 (2 H)	3.73 (2 H)	

<sup>a</sup> Experimental error of  $\pm 1\%$ , except for  $2\cdot^-$  where it is  $\pm 5\%$ . <sup>b</sup> Spectra corresponding to those of the parent radical anion  $1\cdot^-$  (see text). <sup>c</sup> Methylene  $\beta$  protons of alkyl substituents. <sup>d</sup> Assignment uncertain. <sup>e</sup> Numbers of interacting protons are indicated in parentheses.

fluorene (**3**) and its 9-methyl-, 9,9-dimethyl-, and 9,9-diphenyl derivatives (**4**, **5**, and **6**, respectively).<sup>4,5</sup> The values for  $3\cdot^-$  to  $6\cdot^-$ , which are also given in Table II, were remeasured for the present work. They were found not to depend markedly on solvent and/or counterion used.

It is tempting to attribute the spectra b and c of Figure 1 to a radical anion  $1\cdot^-$ , in which the unpaired electron is *localized on one fluorene moiety*, in contrast to the spectrum a representing  $1\cdot^-$  with such an electron *delocalized over both mutually perpendicular moieties*. This interpretation is supported by experiment, since (as will be shown below) the spectra b and c *cannot arise from a triplet dianion of 1 nor from a secondary radical anion*.

The signals ascribed to a ground or low-lying triplet state of spirobifluorene dianion<sup>2</sup> ( $D$  value  $\approx 60$  G) are observed when a solution of **1** is frozen after prolonged reduction (*i.e.*, at the stage where it displays the spectrum b or c). Figure 2 reproduces such signals of the triplet dianion which flank a central absorption due to a

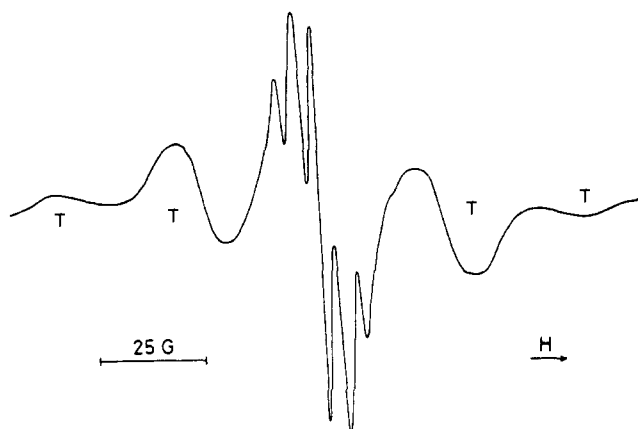
glass spectrum of  $1\cdot^-$ . The latter spectrum is easily identified as b or c, since it still preserves the main hyperfine pattern characteristic of b and c in fluid solution. The fact that it is observed along with the signals of the triplet dianion rules out the possibility that b and c arise from such a dianion. Interestingly, a triplet dianion is also found by esr spectroscopy for 2,2'-di-*n*-propyl-7,7'-diethylspirobifluorene (**2**), but fails to be detected for the fluorenes **3–6** under analogous conditions. This result can be rationalized in terms of double degeneracy expected for the lowest antibonding orbitals of the spirocompounds **1** and **2**.<sup>6</sup>

Formation of a secondary radical anion must also be considered for prolonged contact of **1** with an alkali metal, since spiroconjugated compounds are known to readily undergo bond cleavage at the spirócarbon.<sup>7,8</sup> An example of such a cleavage is provided by potassium

(6) In the tetraalkyl derivative **2**, the deviation from the  $D_{2d}$  symmetry is too slight to effectively remove the degeneracy.

(7) G. Frages and A. S. Dreiding, *Helv. Chim. Acta*, **49**, 552 (1966).

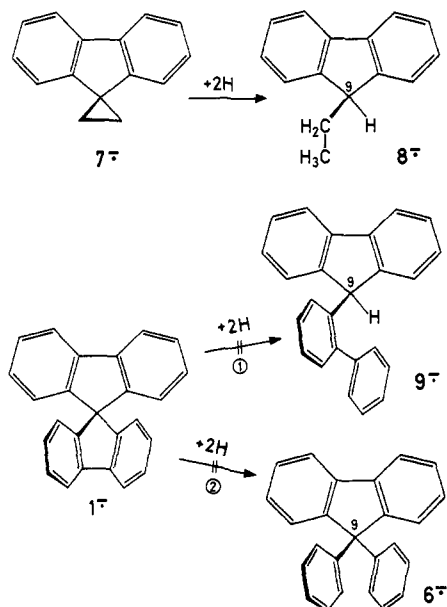
(8) V. Prelog, personal communication.



**Figure 2.** ESR spectrum of spirobifluorene radical anion ( $1\cdot^-$ ) and dianion in glassy solution: solvent, MTHF; counterion,  $K^+$ ; temperature,  $-150^\circ$ . The signals of the triplet dianion are marked by T.

reduction of spiro[cyclopropanefluorene] ( $7$ ) (cf. Experimental Section). The resulting esr spectrum is almost identical with that of 9-methylfluorene radical anion ( $4\cdot^-$ ) and must be due to the 9-ethyl derivative  $8\cdot^-$ . Clearly, the conversion of  $7\cdot^-$  to  $8\cdot^-$  requires scission of one spirocarbon-methylene bond and subsequent abstraction of two hydrogen atoms from the solvent, as indicated by Scheme I. Analogous re-

**Scheme I**



action of  $1\cdot^-$  (denoted ① in Scheme I) would lead to 9-(*o*-biphenyl)fluorene radical anion ( $9\cdot^-$ ) which like  $4\cdot^-$  and  $8\cdot^-$  is expected to exhibit a considerable hyperfine splitting from the 9 proton (Table II). The absence of such a splitting ( $\sim 4$  G) in b and c unequivocally excludes  $9\cdot^-$  as the species giving rise to these spectra.

An alternative type of cleavage (denoted ② in Scheme I) would affect one of the phenyl-phenyl bonds to yield the 9,9-diphenylfluorene radical anion ( $6\cdot^-$ ) after

an addition of two hydrogen atoms. However, the esr spectrum of  $6\cdot^-$  differs significantly from b and c, especially in the coupling constants assigned to the 1,8 and 3,6 protons (Table II). Moreover, prolonged reduction of  $6$  results in the 9-phenylfluorenyl radical dianion,<sup>5</sup> whereas no such species could be detected by esr spectroscopy for  $1$ . The final proof is provided by careful mass spectrometric analysis of the products obtained from MTHF solutions of  $1\cdot^-$  (displaying spectrum c) and  $6\cdot^-$  after admission of air. The finding that these products consist mainly of the regenerated starting materials  $1$  and  $6$ , respectively, not only excludes the conversion of  $1\cdot^-$  to  $6\cdot^-$ , but argues against an appreciable formation of a secondary radical anion during the period of reduction required to obtain the spectra b and c.

Last, but not least, the interpretation of the spectra b and c as those of the primary radical anion  $1\cdot^-$ , but with the unpaired electron localized on one fluorene moiety, is corroborated by the reversibility of the spectral sequence  $a \rightarrow b \rightarrow c$ . When, after a prolonged reaction with potassium, a solution of  $1\cdot^-$  in THF is diluted by an order of magnitude the spectrum c changes to one denoted  $t_3$  in Figure 1 and intermediate between a and b. A similar change is brought about when an equal volume of DME is added to a solution of  $1\cdot^-$  in MTHF.

### Conclusion

An effect which would account for the spin localization in  $1\cdot^-$  is the association of the radical anion with its alkali metal counterion. The passage from a to b and c (Figure 1), which signals such a localization upon prolonged reduction, can thus be rationalized by the increase in the concentration of  $K^+$  or  $Na^+$  accompanying the additional formation of both radical anions  $1\cdot^-$  and triplet dianions.

Since the association between a radical anion and its counterion is enhanced in nonpolar solvents, changing from DMF to DME, THF and MTHF should favor spin localization in  $1\cdot^-$ . This in fact is found experimentally: the less polar the solvent, the greater the preference for b and c over a (Table I).

The slight differences in the hyperfine splittings of b and c can be ascribed to different solvation, b being closer to a spectrum of a "solvent-shared," and c to that of a "contact" ion pair.<sup>9</sup> The tendency of  $1\cdot^-$  to yield the spectrum b rather than c when  $K^+$  is replaced by  $Na^+$  (Table I) is consistent with this assumption, since the latter cations are better solvated than the former.

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(9) N. Hirota and R. Kreilick, *J. Amer. Chem. Soc.*, **88**, 614 (1966); N. Hirota, *J. Phys. Chem.*, **71**, 127 (1967).