263. The Radical Anions of Some Substituted [2.2]Paracyclophanes

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Summary

The radical anions of the following substituted [2.2]paracyclophanes have been characterized by ESR. and ENDOR. spectroscopy: 4,16-dicyano- (***o*-2**), 4,12-dicyano- (***p*-2**), 4,5,12,13-tetracyano- (**3**) and 4,5,12,13-tetrakis(alkoxycarbonyl)-[2.2]paracyclophanes (**4-R**, where R = Me, Et, *i*Pr or *t*Bu is the ester alkyl group); 4,5-bis(methoxycarbonyl)[2.2]paracyclophane-12,13-dicarboxylic anhydride (**5**); [2.2]paracyclophane-4,5:12,13-tetracarboxylic bisanhydride (**6**) and bisimides (**7-R**, where R = H, D, Me or Ph is the substituent at the imide *N*-atom). Comparison of the hyperfine data for these radical anions with those for analogously substituted derivatives of benzene indicates that the most prominent coupling constants are approximately halved on passing from the latter to the former. Lowering of the symmetry, as a consequence of ion pairing, has been observed for the radical anions **4-*i*Pr**$^{\ominus}$ and **4-*t*Bu**$^{\ominus}$ associated with the counterion K$^{\oplus}$ in 1,2-dimethoxyethane at 183 K, but not for **4-Me**$^{\ominus}$ and **4-Et**$^{\ominus}$ under the same conditions. This result suggests that the migration of K$^{\oplus}$ between the preferred sited in two equivalent ion pairs is slowed down by the steric hindrance arising from the bulky *i*Pr and *t*Bu ester groups.

Introduction. - Due to a novel synthetic approach, substituted derivatives of [2.2]paracyclophane (**1**) have become readily available in the last few years [1]. The present paper reports the characteristic data (*g*-factors and hyperfine coupling constants) for the radical anions of some of these derivatives. It is appropriate to arrange the pertinent compounds into four groups:

A) 4,16-Dicyano[2.2]paracyclophane (pseudo-*ortho*; ***o*-2**), 4,12-dicyano[2.2]-paracyclophane (pseudo-*para*; ***p*-2**) and 4,5,12,13-tetracyano[2.2]paracyclophane (**3**).

B) 4,5,12,13-Tetrakis(alkoxycarbonyl)[2.2]paracyclophanes (**4-R**, where R = Me, Et, *i*Pr or *t*Bu is the alkyl group of the esters).

C) 4,5-Bis(methoxycarbonyl)[2.2]paracyclophane-12,13-dicarboxylic anhydride (**5**) and [2.2]paracyclophane-4,5:12,13-tetracarboxylic bisanhydride (**6**) (note that the compound **5** may be regarded as a 'hybrid' of **4-Me** and **6**).

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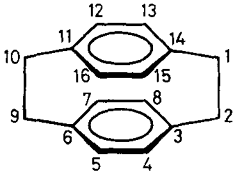
D) [2.2]Paracyclophane-4,5:12,13-tetracarboxylic bisimides (**7-R**, where R = H, D, Me or Ph is the substituent at the imide *N*-atom).



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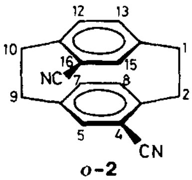
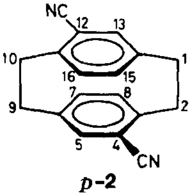
The numbering in the upper benzene ring of **1** is the one proposed by *Vögtle & Neumann* [2]. It allows the use of smaller numbers (12 and 13 instead of 15 and 16) for the substituted positions in **3**, **4-R**, **5**, **6** and **7-R**.

Table 1. *Hyperfine data and g-factors for the radical anions of the cyano derivatives* (group *A*)



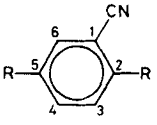
o-**2**

DME/$K^{\oplus}$/183		
$a_{X\mu}$	nX	μ
0.414	2H	7,13
0.252	2H	5,15
0.154	2H	2,10-CH_2-
0.065	2H	
0.050	2H	1,9-CH_2-
0.046	2H	
0.039	2H	8,12
0.100	2N	4,16-C*N*
g = 2.0027		



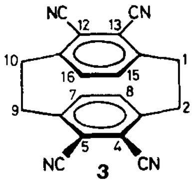
p-**2**

DME/$K^{\oplus}$/183		
$a_{X\mu}$	nX	μ
0.422	2H	7,15
0.284	2H	5,13
0.269	2H	2,10-CH_2-
0.119	2H	
0.048	2H	1,9-CH_2-
0.042	2H	
0.016	2H	8,16
0.112	2N	4,12-C*N*
g = 2.0027		



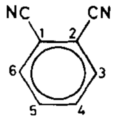
2a-R

R = H			Me		
DMF/$Et_4N^{\oplus}$/213			DME/$K^{\oplus}$/183		
$a_{X\mu}$ [a]	nX	μ	$a_{X\mu}$	nX	μ
0.856	1H	4	0.839	1H	4
0.373	2H	2,6	0.447	1H	6
0.028	2H	3,5	0.313	3H	2-CH_3
0.220	1N	1-C*N*	0.082	3H	5-CH_3
g = 2.0026			0.003	1H	3
			0.228	1N	1-C*N*
			g = 2.0026		



3

DME/$K^{\oplus}$/183		
$a_{X\mu}$	nX	μ
0.213	4H	7,8,15,16
0.053	4H	1,2,9,10-CH_2-
0.040	4H	
0.094	4N	4,5,12,13-C*N*
g = 2.0027		



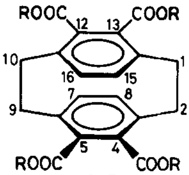
3a

DMF/$Et_4N^{\oplus}$/213		
$a_{X\mu}$ [a]	nX	μ
0.416	2H	4,5
0.036	2H	3,6
0.177	2N	1,2-C*N*
g = 2.0026		

[a] Values agreeing with those reported previously by other workers [3].

Results. - The radical anions *o*-**2**$^{\overset{\cdot}{\ominus}}$, *p*-**2**$^{\overset{\cdot}{\ominus}}$, **3**$^{\overset{\cdot}{\ominus}}$, **4-R**$^{\overset{\cdot}{\ominus}}$, **5**$^{\overset{\cdot}{\ominus}}$, **6**$^{\overset{\cdot}{\ominus}}$ and **7-R**$^{\overset{\cdot}{\ominus}}$ were generated from the respective neutral compounds by electrolysis in *N,N*-dimethylformamide (DMF) with tetraethylammonium perchlorate as the supporting salt and by 'chemical' reduction in 1,2-dimethoxyethane (DME) with potassium. Both methods led to well-defined ESR. spectra which were, in general, better resolved with the use of the electrolytic preparation. However, in the alternative case of the chemical reduction, the analysis of the ESR. spectra could be assisted by the

Table 2. *Hyperfine data and* g*-factors for the radical anions of the alkoxycarbonyl derivatives* (group *B*)

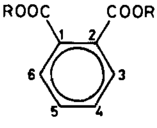


4-R

R =	Me	Et	*i*Pr	*t*Bu		
	DMF/Et$_4$N$^{\oplus}$/213					
	$a_{X\mu}$	$a_{X\mu}$	$a_{X\mu}$	$a_{X\mu}$	nX	μ
	0.194	0.194	0.193	0.192	4H	7,8,15,16
	0.060	0.061	0.063	0.064	4H	1,2,9,10-CH_2-
	0.031	0.031	0.031	0.031	4H	
	0.031				12H	4,5,12,13-COOCH_3
		0.031			8H	4,5,12,13-COOCH_2-
			0.011		4H	4,5,12,13-COOCH<

R =	Me	Et		
	DME/K$^{\oplus}$/183			
	$a_{X\mu}$	$a_{X\mu}$	nX	μ
	0.197	0.197	4H	7,8,15,16
	0.048	0.050	4H	1,2,9,10-CH_2-
	0.035	0.036	4H	
	0.031		12H	4,5,12,13-COOCH_3
		0.030	8H	4,5,12,13-COOCH_2-
	g = 2.0034			

*i*Pr	*t*Bu		
DME/K$^{\oplus}$/183			
$a_{X\mu}$	$a_{X\mu}$	nX	μ
0.258	0.276	2H	7,8
0.150	0.132	2H	15,16
0.104	0.114	2H	2,9-CH_2-
0.021	0.018	2H	
0.059	0.057	2H	1,10-CH_2-
0.004	0.004	2H	
0.021		2H	4,5-COOCH<
g = 2.0034			



4a-R

R =	Me	Et	*i*Pr	*t*Bu		
	DMF/ Et$_4$N$^{\oplus}$/213		MeCN/ Pr$_4$N$^{\oplus}$/298	Me$_2$SO/ Bu$_4$N$^{\oplus}$/298		
	$a_{X\mu}$ [a]	$a_{X\mu}$ [a]	$a_{X\mu}$ [b]	$a_{X\mu}$ [c]	nX	μ
	0.343	0.343	0.347	0.337	2H	4,5
	0.088	0.088	0.082	0.086	2H	3,6
	0.076				6H	1,2-COOCH_3
		0.076			4H	1,2-COOCH_2-
			0.032		2H	1,2-COOCH<
	g = 2.0035					

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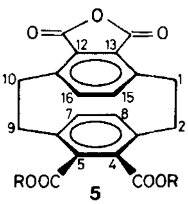
[a] Values agreeing with those reported in [5], which are more elaborate than the data given by other workers [4].

[b] Values taken from [5]; g-factor not reported.

[c] Values taken from [6]; g-factor not reported.

Table 3. *Hyperfine data and g-factors for the radical anions of the carboxylic anhydrides* (group *C*)



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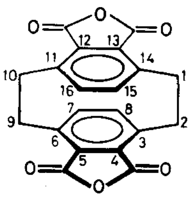
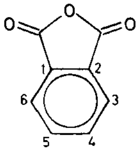
DMF/Et$_4$N$^{\oplus}$/213		
$a_{X\mu}$	nX	μ
0.198	2H	7,8
0.114	2H	15,16
0.023	2H	2,9-CH_2-
0.023	2H	
0.023	6H	4,5-COOCH_3
g = 2.0036		



6

DME/K$^{\oplus}$/183		
$a_{X\mu}$	nX	μ
0.156	4H	7,8,15,16
0.015	4H	1,2,9,10-CH_2-
0.006	4H	
0.332$^{a)}$	4 ^{13}C	3,6,11,14 or 7,8,15,16
g = 2.0038		



6a

DMF/Et$_4$N$^{\oplus}$/213		
$a_{X\mu}$ $^{b)}$	nX	μ
0.258	2H	4,5
0.022	2H	3,6
g = 2.0036		

[a] Value obtained with DMF/Et$_4$N$^{\oplus}$/213.

[b] Values agreeing with those reported previously by other workers [7] [8].

ENDOR. technique which, among other advantages, enabled one to determine proton coupling constants smaller than 0.01 mT.

Tables 1, 2, 3 and *4* collect the experimental data for the radical anions in the groups *A* (*o*-**2**$^{\ominus}$, *p*-**2**$^{\ominus}$ and **3**$^{\ominus}$), *B* (**4-R**$^{\ominus}$), *C* (**5**$^{\ominus}$ and **6**$^{\ominus}$) and *D* (**7-R**$^{\ominus}$), respectively. The conditions (solvent/counterion/temperature in K), under which the data were acquired, are indicated in the top lines of each entry. The columns underneath contain the coupling constants $a_{X\mu}$ in mT, the numbers n of nuclei giving rise to them, and the positions μ to which they are assigned. This assignment is, to a large extent, based on comparison with the hyperfine data for the radical anions of analogously substituted benzene derivatives: *o*-**2**$^{\ominus}$ and *p*-**2**$^{\ominus}$ *vs.* benzonitriles (**2a-R**$^{\ominus}$), **3**$^{\ominus}$ *vs.* 1,2-dicyanobenzene (**3a**$^{\ominus}$), **4-R**$^{\ominus}$ *vs.* phthalic diesters (**4a-R**$^{\ominus}$), **6**$^{\ominus}$ *vs.* phthalic anhydride (**6a**$^{\ominus}$), and **7-R**$^{\ominus}$ *vs.* phthalic imides (**7a-R**$^{\ominus}$). The coupling constants $a_{X\mu}$ for the reference species are included in *Tables 1-4*, along with the values for the radical anions of the corresponding substituted [2.2]paracyclophanes. With several specified exceptions, they have also been obtained in our laboratory. The g-factors are given at the end of each entry for the radical anions of substituted [2.2]paracyclophanes and for those of the benzene derivatives studied or reinvestigated in the present work. In the case of the data taken from literature, such factors have not been available. The experimental errors in the values $a_{X\mu}$ measured in our laboratory are ±0.002 and ±0.001 mT for $a_{X\mu}$ larger and smaller than 0.1 mT, respectively, while the accuracy in the g-factors is ±0.0001.

In the groups *A, C* and *D* (*Tables 1, 3* and *4*) only the data for chemically prepared radical anions (DME/K$^{\oplus}$ as the solvent/counterion) are given[2]), since the dif-

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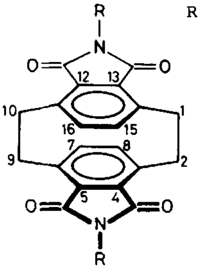
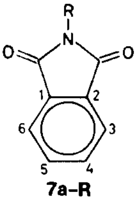
[2]) For **5**$^{\ominus}$, the analysis of the spectrum taken with DME/K$^{\oplus}$ was rendered difficult by the presence of a secondary radical anion. Thus, exceptionally in this case, the data obtained with DMF/Et$_4$N$^{\oplus}$ are given instead *(Table 3)*.

Table 4. *Hyperfine data and g-factors for the radical anions of the carboxylic imides* (group *D*)



7-R

R = H	Me	Ph		
DME/K$^{\oplus}$/183				
$a_{X\mu}$	$a_{X\mu}$	$a_{X\mu}$	nX	μ
0.154	0.150	0.150	4H	7,8,15,16
0.013	0.012	0.012	4H	1,2,9,10-CH_2-
0.005	0.005	0.003	4H	
0.101	0.107	0.103	2N	4,5:12,13-$(CO)_2N$-
0.013[a]			2H	4,5:12,13-$(CO)_2NH$
	0.038		6H	4,5:12,13-$(CO)_2NCH_3$
		0.012	6H[b]	4,5:12,13-$(CO)_2NPh$
g = 2.0040				



7a-R

R = H		Me	Ph		
DMF/ K$^{\oplus}$/ 213	MeOH/ K$^{\oplus}$/ 293	Me_2SO/ $Bu_4N^{\oplus}$/ 293	DMF/ $Bu_4N^{\oplus}$/ 231		
$a_{X\mu}$[c]	$a_{X\mu}$[d]	$a_{X\mu}$[e]	$a_{X\mu}$[f]	nX	μ
0.243	0.202	0.241	0.258	2H	4,5
0.021	0.056	0.024	0.032	2H	3,6
0.243	0.288	0.254	0.258	1N	1,2-$(CO)_2N$-
0.045	0.056[g]			1H	1,2-$(CO)_2NH$
		0.090		3H	1,2-$(CO)_2NCH_3$
			0.032	3H[b]	1,2-$(CO)_2NPh$
g = 2.0038					

[a] For R = D, value replaced by unresolved deuteron splitting (~0.002 mT).

[b] Presumably, phenyl *ortho*- and *para*-protons.

[c] Values agreeing with those reported previously by other workers [7] [8].

[d] Values depending strongly on experimental conditions (solvent).

[e] Values taken from [8]; *g*-factor not reported.

[f] Values taken from [7]; *g*-factor not reported.

[g] For R = D (solvent MeOD), value replaced by $a_{D\mu}$ = 0.009 mT.

ferences between the coupling constants found by this method and those observed upon electrolysis (DMF/$Et_4N^{\oplus}$) do not exceed the experimental error. On the other hand, such a statement does not hold for the radical anions in group *B*, particularly for **4-*i*Pr**$^{\ominus}$ and **4-*t*Bu**$^{\ominus}$. Thus the values $a_{X\mu}$ obtained by the use of both methods are listed for this group *(Table 2)*.

As illustration, *Figures 1, 2* and *3* show the ESR. and ENDOR. spectra of the radical anions ***p*-2**$^{\ominus}$, **4-*t*Bu**$^{\ominus}$ and **7-Me**$^{\ominus}$ belonging to three different groups (*A, B* and *D*, respectively).

Discussion. - Two major comments on the experimental data presented in *Tables 1-4* seem appropriate.

1) The relationship, expected for the radical anions of the symmetrically substituted [2.2]paracyclophanes (*o*-**2**, *p*-**2**, **3**, **4-R**, **6** and **7-R**) and those of the analogous benzene derivatives (**2a-R**, **3a**, **4a-R**, **6a** and **7a-R**), is, on the whole, borne out by the hyperfine data. Thus on passing from the latter to the former, the most prominent coupling constants a_{X_μ} of the corresponding nuclei X (X = ^{1}H or ^{14}N) are halved (group *A*) or decreased by a factor of 1.6 to 1.8 (*B* to *D*). Nevertheless, the substantial differences in the value a_{H_μ} found for the radical anions of the two isomeric dicyano derivatives, *o*-**2** and *p*-**2**, show that the way, in which the two equivalent aromatic moieties are compounded, is important.

2) In general, association of *o*-**2**$^{\overset{\cdot}{\ominus}}$, *p*-**2**$^{\overset{\cdot}{\ominus}}$, **3**$^{\overset{\cdot}{\ominus}}$, **4-R**$^{\overset{\cdot}{\ominus}}$, **6**$^{\overset{\cdot}{\ominus}}$ and **7-R**$^{\overset{\cdot}{\ominus}}$ with their counterions (ion pairing) does not lower the apparent symmetry of the radical anions (C_{2h} or C_{2v}) under the conditions of our experiments (DMF/Et$_4$N$^{\oplus}$/213 or DME/K$^{\oplus}$/183 as the solvent/counterion/temperature in K). A reduced symmetry (C_s) is expected for the ion pairs formed by these radical anions with their counterions, if, as in the case of the parent **1**$^{\overset{\cdot}{\ominus}}$ [9], the cation is situated in the proximity of

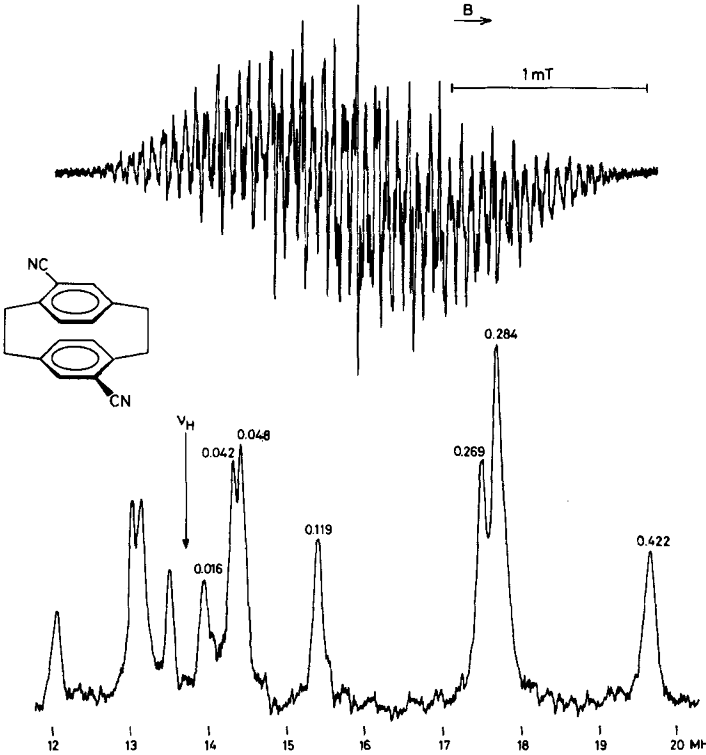


Fig. 1. *ESR. and ENDOR. spectra of the radical anion of 4,12-dicyano[2.2]paracyclophane* (*p*-**2**). Solvent DME, counterion K$^{\oplus}$, temp. 183 K. The numbers above the ENDOR. proton signals represent the pertinent coupling constants in mT. ν_H = frequency of the free proton.

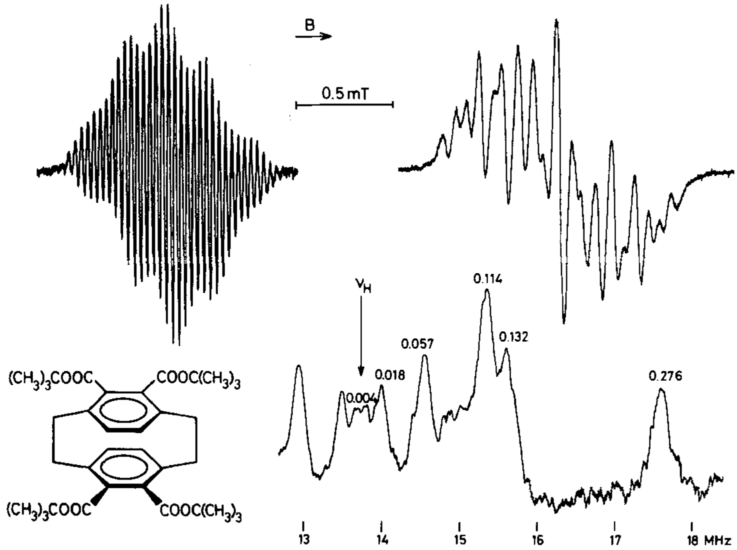


Fig. 2. *ESR. and ENDOR. spectra of the radical anion of 4,5,12,13-tetrakis(*t*-butoxycarbonyl)[2.2]paracyclophane* (**4-*t*Bu**). ESR. spectrum left: solvent DMF, counterion Et$_4$N$^{\oplus}$, temp. 213 K. ENDOR. and ESR. spectrum right: solvent DME, counterion K$^{\oplus}$, temp. 183 K. The numbers above the ENDOR. proton signals represent the pertinent coupling constants in mT. ν_H = frequency of the free proton.

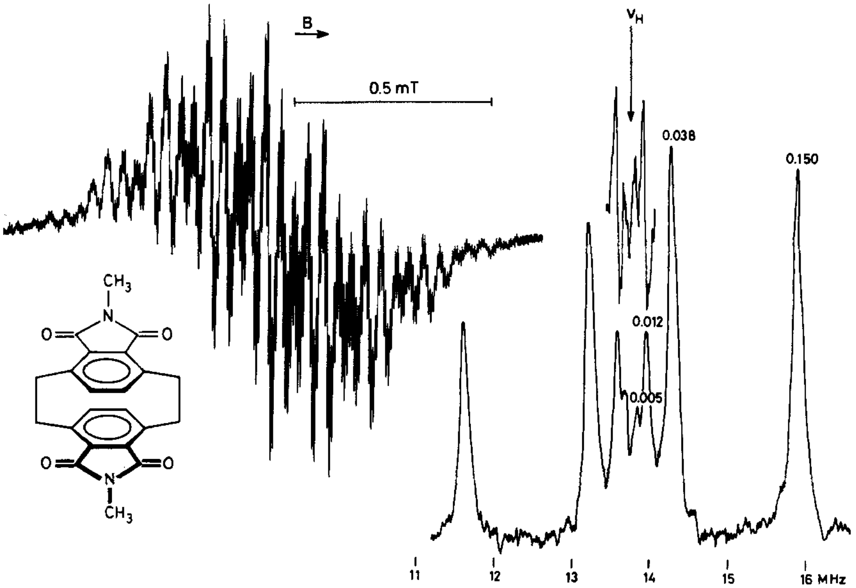


Fig. 3. *ESR. and ENDOR. spectra of the radical anion of* N,N'*-dimethyl[2.2]paracyclophane-4,5:12,13-tetracarboxylic bisimide* (**7-Me**). ESR.: solvent DMF, counterion Et$_4$N$^{\oplus}$, temp. 213 K. ENDOR.: solvent DME, counterion K$^{\oplus}$, temp. 183 K. The numbers above the ENDOR. proton signals represent the pertinent coupling constants in mT. The upper insert (close to the free proton frequency ν_H) shows the ENDOR. curve in its derivative form which renders the signals due to the protons with the smallest coupling constant (0.005 mT) more evident.

only one of the two equivalent aromatic moieties. Thus, the failure to observe the lower symmetry implies that the interconversion between such an ion pair and its counterpart, in which the cation occupies an equivalent site at the second moiety, is fast on the hyperfine time-scale ($> 10^8 s^{-1}$). Consequently, one observes the averaged values a_{X_μ} of the two equivalent ion pairs [10]. Notable exceptions to the rapid interconversion are, in the present work, the radical anions **4-*i*Pr**$^{\ominus}$ and **4-*t*Bu**$^{\ominus}$, which, with $K^{\oplus}$ in DME at 183 K, give rise to ESR. and ENDOR. spectra exhibiting the reduced symmetry and the coupling constants characteristic of an individual ion pair. It appears that the interconversion of two equivalent ion pairs becomes slower on going from **4-Me**$^{\ominus}$ and **4-Et**$^{\ominus}$ to **4-*i*Pr**$^{\ominus}$ and **4-*t*Bu**$^{\ominus}$, *i.e.*, with the increasing size of the ester alkyl group R. This finding is readily rationalized as follows: As suggested by the studies of the radical anions of the phthalic diesters (**4a-R**$^{\ominus}$) [5], a preferred site of the cation in its ion pair with **4-R**$^{\ominus}$ should be close and symmetrically positioned to both *ortho* alkoxycarbonyl substituents of one benzene ring. Since the interconversion of ion pairs is tantamount to the migration of the counterion between two such equivalent sites [10], the retarding effect of the bulky *i*Pr and *t*Bu groups can be attributed to the steric hindrance caused by these groups to the migration in question. It is also interesting to note, that the rotation of R about the C–O ester bond is unrestricted on the hyperfine time-scale for R = Me and Et ($a_{H(4,5,12,13\text{-}CH_3)} = a_{H(4,5,12,13\text{-}CH_2-)} = 0.031$ mT), whereas it is not so for R = *i*Pr ($a_{H(4,5,12,13\text{-}CH<)} = 0.011$ mT).

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