158. Rearrangements of Radical Cations of [2.2]Paracyclophanes and of a Bridged [14]Annulene to those of Pyrenes: An ESR and ENDOR Study

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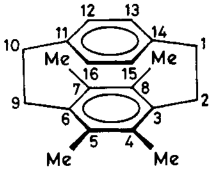
ESR and ENDOR studies have been carried out on the radical cations obtained consecutively by reaction of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**4**) with $AlCl_3$ in CH_2Cl_2. The primarily formed **4**$^{+\cdot}$ rearranges at 253 K to the radical cation(s) of 1,6- (**5a**) and/or 1,8-dimethylpyrene (**5b**). At 323 K, the spectra of **5a**$^{+\cdot}$/**5b**$^{+\cdot}$ are replaced by that of the highly persistent radical cation of 1,3,6,8-tetramethylpyrene (**6**). Surprisingly, **6**$^{+\cdot}$ is also the only observable paramagnetic product resulting from a treatment of 4,5,7,8- (**1**), 4,7,13,16- (**2**), and 4,5,12,13-tetramethyl[2.2]paracyclophane (**3**) with $AlCl_3$ in CH_2Cl_2 at 353 K. The structures of the intermediates in the rearrangement [**1**$^{+\cdot}$, **2**$^{+\cdot}$, **3**$^{+\cdot}$] → **6**$^{+\cdot}$ are discussed.

Introduction. – It was reported a number of years ago [1] that electrolytic oxidation of 4,5,7,8-tetramethyl[2.2]paracyclophane (5,6,15,16-tetramethyltricyclo[$8.2.2.2^{4,7}$]hexadeca-4,6,10,12,13,15-hexaene; **1**) in $CH_2Cl_2/CF_3COOH/(CF_3CO)_2O$ (10:1:1) at 193 K leads to the dimeric radical cation $\mathbf{1}_2^{+\cdot}$. Under more rigorous conditions, such as dissolution of **1** in molten $SbCl_3$ or its reaction with $AlCl_3$ in CH_2Cl_2 at 353 K, another well-defined ESR spectrum was observed [2]; this has been attributed to the monomeric radical cation **1**$^{+\cdot}$. Later on, however, doubt was cast on this interpretation, because an analogous treatment of the isomeric 4,7,13,16-tetramethyl[2.2]paracyclophane (5,11,13,15-tetramethyltricyclo[$8.2.2.2^{4,7}$]hexadeca-4,6,10,12,13,15-hexaene; **2**), and 4,5,12,13-tetramethyl[2.2]paracyclophane (5,6,11,12-tetramethyltricyclo[$8.2.2.2^{4,7}$]hexadeca-4,6,10,12,13,15-hexaene; **3**) with $AlCl_3$ in CH_2Cl_2 resulted in an ESR spectrum [3][4] which was identical with that previously attributed to **1**$^{+\cdot}$. The structure of the radical cation giving rise to this spectrum is disclosed in the present paper which deals with oxidation of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**4**) by $AlCl_3$ in CH_2Cl_2.



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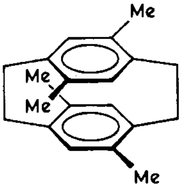

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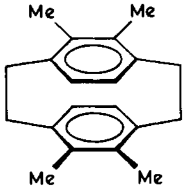

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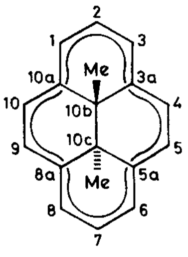

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Results and Discussion. – *ESR and ENDOR Spectra.* The bridged [14]annulene **4** reacted readily with $AlCl_3$ in CH_2Cl_2 at 193 K to form the primary radical cation $\mathbf{4}^{\dot{+}}$. The ESR spectrum of $\mathbf{4}^{\dot{+}}$ obtained under these conditions (*Fig. 1* top; total width 2.02 mT) closely resembled that observed previously upon dissolution of **4** in conc. H_2SO_4 at 298 K [5]. When the solution of $\mathbf{4}^{\dot{+}}$ in CH_2Cl_2 was allowed to warm up to 253 K, the spectrum of $\mathbf{4}^{\dot{+}}$ gradually changed into a new one arising from a secondary radical cation $\mathbf{5}^{\dot{+}}$ (*Fig. 1* centre; total width 5.90 mT). Further rise of the temperature to 323 K caused the spectrum of $\mathbf{5}^{\dot{+}}$ to be replaced by that of a highly persistent, tertiary radical cation $\mathbf{6}^{\dot{+}}$ (*Fig. 1* bottom; total width 7.88 mT). It is important to note that *this spectrum is the same as that observed previously upon oxidation of either isomeric tetramethyl[2.2]paracyclophane* **1**, **2**, and **3** with $AlCl_3$ in CH_2Cl_2 at 353 K [2–4].

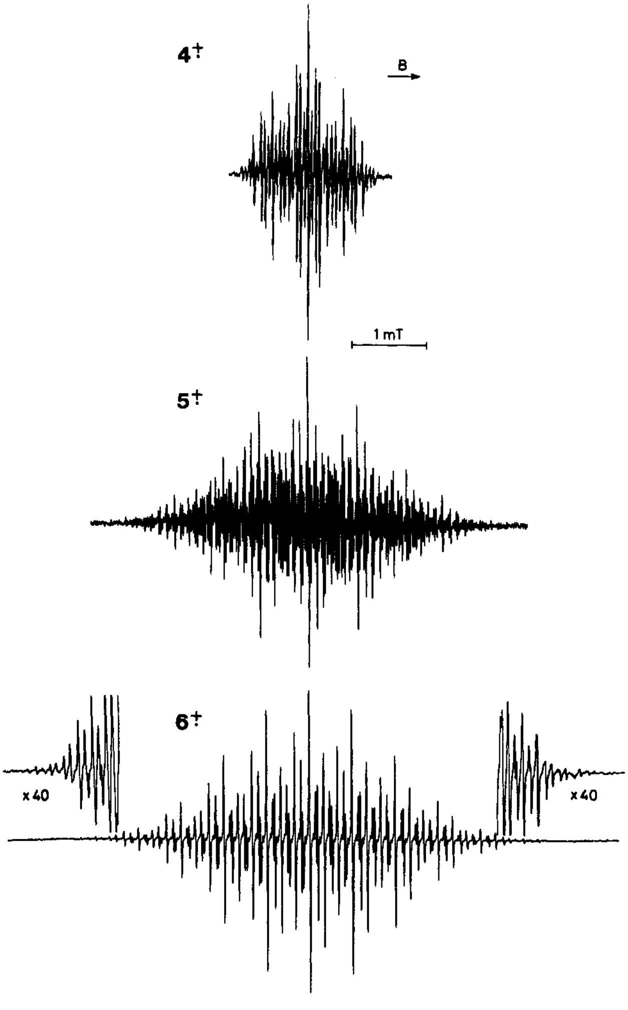


Fig. 1. *ESR spectra of the primary* ($\mathbf{4}^{\dot{+}}$), *secondary* ($\mathbf{5}^{\dot{+}}$), *and tertiary* ($\mathbf{6}^{\dot{+}}$) *radical cations from* trans-*10b,10c-dimethyl-10b,10c-dihydropyrene* (**4**). Solvent: CH_2Cl_2. Temp.: 193 ($\mathbf{4}^{\dot{+}}$), 273 ($\mathbf{5}^{\dot{+}}$), and 303 K ($\mathbf{6}^{\dot{+}}$).

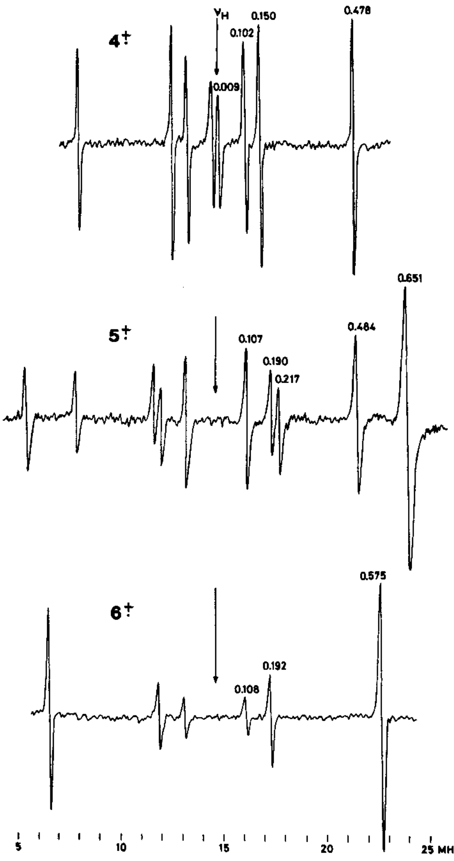


Fig. 2. *^{1}H-ENDOR spectra of the primary* ($\mathbf{4}^{+\cdot}$)*, secondary* ($\mathbf{5}^{+\cdot}$)*, and tertiary* ($\mathbf{6}^{+\cdot}$) *radical cations from* **4**. Solvent: CH_2Cl_2. Temp.: 193 ($\mathbf{4}^{+\cdot}$) and 203 ($\mathbf{5}^{+\cdot}$ and $\mathbf{6}^{+\cdot}$). The numbers [mT] are the proton coupling constants $|a_{H\mu}|$ associated with the ENDOR signals.

Analysis of the ESR spectra (*Fig. 1*) and the corresponding ^{1}H-ENDOR spectra (*Fig. 2*) yielded the coupling constants $a_{H\mu}$ listed in *Table 1*. The signs of these values were determined by general TRIPLE resonance (which provided the relative signs [6]), assuming that the largest coupling constants are positive for the Me β-protons and negative for the ring α-protons. The assignments to individual positions μ, wherever not evident from experiment, have been based on MO calculations which in the case of $\mathbf{5}^{+\cdot}$ and $\mathbf{6}^{+\cdot}$ are bound with the identification of these radical cations.

Structures of $\mathbf{5}^{+\cdot}$ *and* $\mathbf{6}^{+\cdot}$. *Table 2* gives the proton coupling constants $a_{H\mu}$ calculated for $\mathbf{4}^{+\cdot}$ and the radical cations of 1,6- (**5a**) and 1,8-dimethylpyrene (**5b**), and 1,3,6,8-tetramethylpyrene (**6**). The notation $\mathbf{5a}^{+\cdot}$, $\mathbf{5b}^{+\cdot}$, and $\mathbf{6}^{+\cdot}$ used for these radical cations in *Table 2* is justified by the excellent agreement of the theoretical values with their experimental counterparts (*Table 1*). It is evident that the structure of $\mathbf{5}^{+\cdot}$ is not quite unambiguous, because the coupling constants predicted for the radical cations of the two dimethylpyrenes

5a and **5b** are too similar to allow a clear-cut distinction. Without further evidence, **5**$^{\dot{+}}$ must, thus, be regarded as either **5a**$^{\dot{+}}$ or **5b**$^{\dot{+}}$ or a mixture of both; it will henceforth be represented by **5a**$^{\dot{+}}$/**5b**$^{\dot{+}}$. In contrast, there is little ambiguity with respect to the structure of **6**$^{\dot{+}}$. Nevertheless, considering the importance of this radical cation as the only observable paramagnetic product in the oxidation of the tetramethyl[2.2]paracyclophanes **1**, **2**, and **3**, its identity has been corroborated by the synthesis of the hitherto unknown 1,3,6,8-tetramethylpyrene. The ESR and ENDOR spectra of the radical cation generated from this compound by reaction with $AlCl_3$ in CH_2Cl_2 at 298 K are identical with those of **6**$^{\dot{+}}$ in *Figs. 1* and *2*.

Rearrangement of **4**$^{\dot{+}}$ *to* **5a**$^{\dot{+}}$/**5b**$^{\dot{+}}$ *and to* **6**$^{\dot{+}}$ (*Scheme 1*). The conversion of **4**$^{\dot{+}}$ to **5a**$^{\dot{+}}$/**5b**$^{\dot{+}}$ is fully analogous to that of the unsubstituted *trans*-10b,10c-dihydropyrene into pyrene [9] (see also [10] for the corresponding radical anions). It necessarily involves intramolecular shift of the two Me groups from the 'inner' to the 'outer' positions of the carbon framework, the 1,6- or 1,8-dialkyl substitution being particularly effective in stabilizing

Table 1. *Proton Coupling Constants,* a_{H_μ} [mT][a]), *Observed for the Primary* (**4**$^{\dot{+}}$), *Secondary* (**5**$^{\dot{+}}$), *and Tertiary* (**6**$^{\dot{+}}$) *Radical Cations from* trans-*10b,10c-Dimethyl-10b,10c-dihydropyrene* (**4**)[b])

4$^{\dot{+}}$		**5**$^{\dot{+}}$		**6**$^{\dot{+}}$	
$a_{H\mu}$	μ[c])	$a_{H\mu}$	μ[c])	$a_{H\mu}$	μ[c])
+0.102(4 H)	1,3,6,8	+0.651(6 H)[d])	1,6 or 1,8	+0.575(12 H)[d])	1,3,6,8
−0.478(2 H)	2,7	+0.107(2 H)	2,7	+0.108(2 H)	2,7
−0.150(4 H)	4,5,9,10	−0.484(2 H)	3,8 or 3,6	−0.192(4 H)	4,5,9,10
+0.009(6 H)[d])	10b,10c	−0.190(2 H)	4,9 or 4,5		
		−0.217(2 H)	5,10 or 9,10		

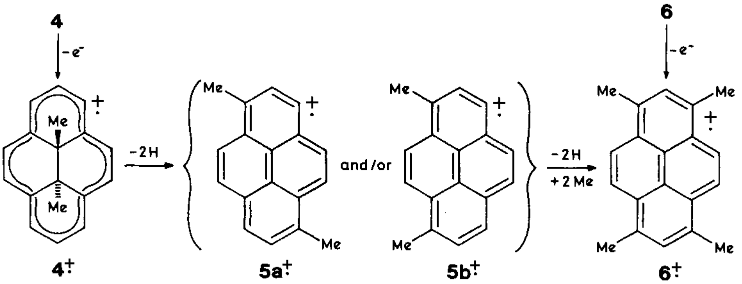
[a]) Exper. error: ±0.001 and ±0.002 mT for $|a_{H\mu}|$ smaller and larger, respectively, than 0.25 mT. [b]) The g-factor is throughout 2.0026±0.0001. [c]) See text for the assignments of $a_{H\mu}$ to positions μ. [d]) Me protons.

Table 2. *Proton Coupling Constants,* a_{H_μ} [mT], *Calculated for the Radical Cations of 10b,10c-Dimethyl-10b,10c-dihydropyrene* (**4**), *1,6- and 1,8-Dimethylpyrenes* (**5a** and **5b**, respectively), *and 1,3,6,8-Tetramethylpyrene* (**6**)[a])

4$^{\dot{+}}$		**5a**$^{\dot{+}}$		**5b**$^{\dot{+}}$		**6**$^{\dot{+}}$	
μ	$a_{H\mu}$	μ	$a_{H\mu}$	μ	$a_{H\mu}$	μ	$a_{H\mu}$
1,3,6,8	+0.12	1,6	+0.65	1,8	+0.64	1,3,6,8	+0.59
2,7	−0.46	2,7	+0.12	2,7	+0.12	2,7	+0.13
4,5,9,10	−0.14	3,8	−0.43	3,6	−0.43	4,5,9,10	−0.22
		4,9	−0.22	4,5	−0.22		
		5,10	−0.24	9,10	−0.23		

[a]) π-Spin populations ρ_μ at the carbon centres μ were calculated by the *Hückel-McLachlan* procedure (λ = 1.2) [7] whereby **4** was considered as a bridged 14-membered π-perimeter. A *Coulomb* parameter $\alpha - 0.2\beta$ was used for the alkyl bridged (μ = 3a,5a,8a,10a in **4**$^{\dot{+}}$) or Me substituted centres (μ = 1,6 in **5a**$^{\dot{+}}$, 1,8 in **5b**$^{\dot{+}}$, and 1,3,6,8 in **6**$^{\dot{+}}$). The ρ_μ values were converted into the coupling constants $a_{H\mu}$ by the relations $a_{H\mu} = -2.5\text{mT}\cdot\rho_\mu$ for the ring α-protons and $a_{H\mu} = +3.4\text{mT}\cdot\rho_\mu$ for the β-protons of Me substituents at the centres μ (see, *e.g.* [8]).

Scheme 1



the radical cation2). At higher temperatures, further intermolecular shifts of the Me groups evidently lead to a disproportionation of **5a**$^{+\cdot}$/**5b**$^{+\cdot}$ to **6**$^{+\cdot}$ and radical cations of less substituted pyrenes. Only the thermodynamically and kinetically by far most stable **6**$^{+\cdot}$, which has the Me groups in 1,3,6,8-positions2), gives rise to observable ESR and ENDOR spectra under the experimental conditions used in the present work.

Rearrangement of **1**$^{+\cdot}$, **2**$^{+\cdot}$, *and* **3**$^{+\cdot}$ *to* **6**$^{+\cdot}$ is more intricate than that of **4**$^{+\cdot}$ to **6**$^{+\cdot}$, because starting from **1**, **2**, and **3** no paramagnetic species are detected by ESR spectroscopy, except the final product **6**$^{+\cdot}$. It is now clear that the spectrum previously attributed to the monomeric radical cation **1**$^{+\cdot}$ [2] is, in fact, due to **6**$^{+\cdot}$ and that all three isomeric tetramethyl[2.2]paracyclophanes **1**, **2**, and **3** do not form persistent radical cations upon oxidation with $AlCl_3$ in CH_2Cl_2. The conversion of these short-lived radical cations into **6**$^{+\cdot}$ must proceed *via* several intermediates. A likely reaction sequence is formulated in *Scheme 2* and discussed below.

When **1** and **3** are treated with $TiCl_4$/HCl in CH_2Cl_2 they isomerize to the sterically more favoured **2** [12] in which the two Me substituents are crossed. An analogous rearrangement should occur with $AlCl_3$ in $CH_2Cl_2$3), presumably after the formation of the corresponding radical cations, **1**$^{+\cdot}$ → **2**$^{+\cdot}$ ← **3**$^{+\cdot}$. Such an isomerization would account for the finding that the same paramagnetic product (**6**$^{+\cdot}$) is obtained, irrespective of the starting material **1**, **2** or **3**. In the presence of $AlCl_3$3), further rearrangement of **2**$^{+\cdot}$ into the radical cation of 4,6,12,15-tetramethyl[2.2]metaparacyclophane (5,7,12,14-tetramethyltricyclo[9.2.2.$1^{4,8}$]hexadeca-4,6,8(16),11,13,14-hexaene; **7**) is indicated by the finding that several [2.2]paracyclophanes isomerize to their metapara-analogues by reaction with $AlCl_3$/HCl in CH_2Cl_2 [13]. Conversion of the non-persistent **7**$^{+\cdot}$ into **6**$^{+\cdot}$ requires the intermediacy of two further short-lived radical cations, namely those of 4,6,12,14-tetramethyl[2.2]metacyclophane (5,7,12,14-tetramethyltricyclo[9.3.1.$1^{4,8}$]hexadeca-1(15),4,6,8(16),11,13-hexaene; **8**) and 1,3,6,8-tetramethyl-4,5,9,10-tetrahydropyrene (**9**), the cyclization product of **8**$^{+\cdot}$ (for analogous rearrangements, see [14]).

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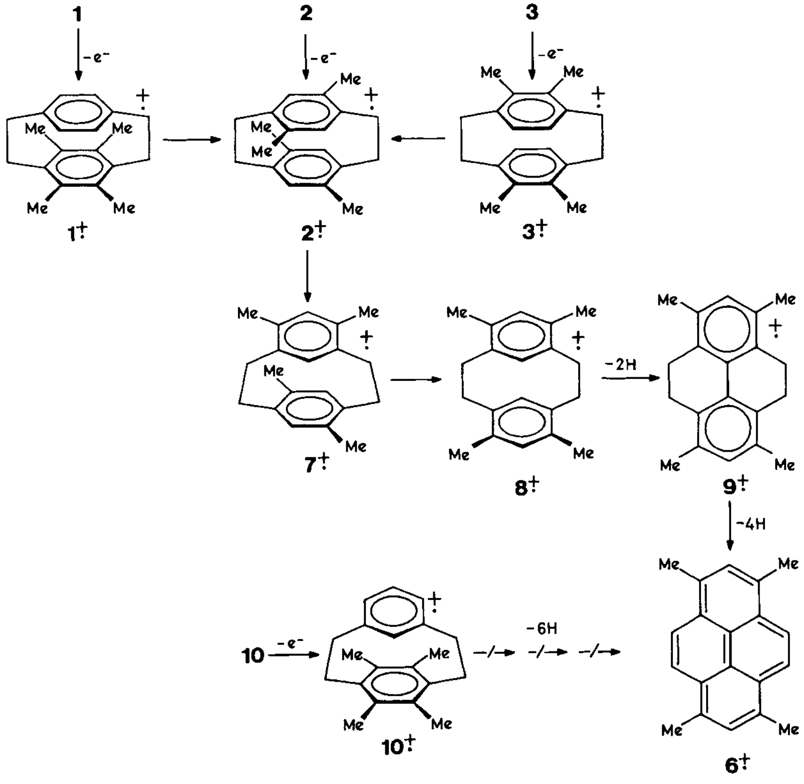
2) The C-atoms in the 1,3,6,8-positions of the pyrene radical cation bear by far the largest π-charge and spin populations [8] [11].

3) Catalytically active traces of HCl are certainly present in the CH_2Cl_2 solutions used for oxidation of **1**, **2**, **3**, and **4**; they arise from reaction of $AlCl_3$ with protic impurities which are difficult to remove completely from the solvent.

It is noteworthy that no ESR spectrum could be observed when the hitherto unknown 12,13,15,16-tetramethyl[2.2]metaparacyclophane (12,13,14,15-tetramethyltricyclo-[9.2.2.$1^{4,8}$]hexadeca-4,6,8(16),11,13,14-hexaene; **10**), which was synthesized in this laboratory, reacted with $AlCl_3$ in CH_2Cl_2 at 353 K. The failure to detect the highly persistent $\mathbf{6}^{+\cdot}$ as the final paramagnetic product in the oxidation of **10** indicates that the primarily formed and (expectedly unstable) radical cation $\mathbf{10}^{+\cdot}$ is not an intermediate in the rearrangement of $\mathbf{1}^{+\cdot}$ to $\mathbf{6}^{+\cdot}$. This conclusion is consistent with *Scheme 2*.

Scheme 2



Experimental. – *Source of Compounds.* The syntheses of **1** [2], **2** [12][15], **3** [16], and **4** [9] have been described elsewhere. Compound **6** was prepared *via* 5,7,14,16-tetramethyl-2,11-dithia[3.3]metacyclophane (6,8,14,16-tetramethyl-3,11-dithiatricyclo[11,3,1,$1^{5,9}$]octadeca-1(17),5,7,9(18),13,15-hexaene) and 4,6,12,14-tetramethyl[2.2]metacyclophane-1,9-diene (5,7,12,14-tetramethyltricyclo[9.3.1.$1^{4,8}$]hexadeca-1(15),2,4,6,8(16),9,11,13-octaene), according to a procedure introduced by *Mitchell* and *Boekelheide* [9]. Synthesis of **10** was accomplished by coupling 1,3-bis(bromomethyl)benzene [17] with the K salt of 2,3,5,6-tetramethyl-1,4-bis(mercaptomethyl)benzene [2] and expulsion of the two S-atoms from the thus formed 14,15,17,18-tetramethyl-2,11-dithia[3.3]metaparacyclophane (14,15,16,17-tetramethyl-3,11-dithiatricyclo[11.2.2.$1^{5,9}$]octadeca-5,7,9(18),13,15,16-hexaene) [17].

Instrumental. The ESR spectra were taken on *Varian-E9* instrument, while *Bruker ESP-300* spectrometer served for the ENDOR and TRIPLE-resonance studies.

Appendix. – The radical anion ($\mathbf{6}^{\bar{\cdot}}$) of 1,3,6,8-tetramethylpyrene (**6**), generated from the neutral compound by K in 1,2-dimethoxyethane has also been characterized with the use of ESR, ENDOR, and TRIPLE-resonance spectroscopy (T = 203 K). The largest (undoubtedly positive) coupling constant $a_{H\mu}$, due to the 12 Me β-protons (μ = 1,3,6,8), is +0.468±0.002 mT. The ring α-protons have $a_{H\mu}$ values of –0.217±0.001 (4 H at μ = 4,5,9,10) and +0.100±0.001 mT (2 H at μ = 2,7). The g-factor is 2.0027±0.0001.

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