2c after CAD ionization). Our results strongly suggest that the observed $M^{+\cdot}$ is $CH_3Cl^{+\cdot}$ rather than $CH_2ClH^{+\cdot}$ and that the observed $HCl^{+\cdot}$ arises from fragmentation prior to CAD ionization.

Conclusions

We have shown in this paper how theory can aid in the design of NRMS experiments in two important ways. In the first place, through its ability to provide detailed potential energy surfaces, theory can suggest which systems might be suitable (and which might be unsuitable) targets for an NRMS investigation. And secondly, through its ability to predict neutralization energies, theory can suggest which metals might be most appropriate for the neutralization step of the experiment.

Our calculations predict in particular that the refined[24] NRMS experiment may provide an excellent means of establishing the stability of the prototype phosphonium ylide (CH_2PH_3). The sulfonium ylide (CH_2SH_2) should survive the NRMS experiment, but the CAD spectrum is likely to be contaminated by fragments arising from rearrangement and dissociation products of CH_2SH_2. We predict that the chloronium ylide (CH_2ClH) will dissociate and/or rearrange when formed by neutralization of $CH_2ClH^{+\cdot}$.

Acknowledgment. We are indebted to Professor F. W. McLafferty for a preprint of his paper which inspired the present study and to Professor R. F. Porter for helpful correspondence.

Registry No. 1a, 593-54-4; **1b**, 74-93-1; **1c**, 74-87-3; **2a**, 36429-11-5; **4a**, 91391-14-9; **4b**, 53369-41-8; **4c**, 12538-71-5; **5a**, 56898-66-9; **5b**, 63933-47-1; **5c**, 81255-84-7.

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[25] The neutral fragments could in principle arise from dissociation of the neutralized parent (e.g., $CH_2ClH \rightarrow CH_2 + ClH$) or from dissociation of $CH_2ClH^{+\cdot}$ through collision with the metal vapor. We favor the latter possibility because of the large energy defect which would be involved in neutralization of $CH_2ClH^{+\cdot}$ with Hg or Zn (see text).

Interplay of Homoconjugative, Inductive, and Hyperconjugative Perturbations in 1,6:8,13-Bridged [14]Annulenes. An ESR Study of the Radical Cations

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Contribution from Physikalisch-Chemisches Institut der Universität Basel, 4056 Basel, Switzerland. *Received March 5, 1984*

Abstract: The radical cations of the following bridged [14]annulenes have been studied by ESR spectroscopy: 1,6:8,13-propane-1,3-diylidene[14]annulene (**1**) and its 7,14-dimethyl (**2**), 15-methyl (**3**), 17-oxo (**4**), and 17-oxo-15,16-dimethyl (**5**) derivatives, and 1,6:8,13-ethanediylidene[14]annulene (**6**) and its 15-methyl (**7**) and 15,16-dimethyl (**8**) derivatives. On passing from $\mathbf{1}^{+\cdot}$ to $\mathbf{6}^{+\cdot}$, there is a striking change in the nodal properties of the singly occupied orbital. This change has been rationalized in terms of the delicate balance of perturbations exerted by the bridging alkanediylidene group on the pair of degenerate HOMO's in the 14-membered π perimeter. Whereas for **1** homoconjugation is most effective in removing the degeneracy of the perimeter HOMO's, the energetic sequence of these MO's in **6** is dominated by inductive and hyperconjugative perturbations. Strong hyperconjugative interaction in $\mathbf{6}^{+\cdot}$ manifests itself by the large β-proton coupling constant of 2.815 mT, which is the prominent feature in the ESR spectrum of this radical cation.

The 1,6:8,13-bridged [14]annulenes[1] represent an interesting series of compounds, because the variety of the bridging alkanediylidene groups enables one to study diverse effects of such groups on the geometry and electronic structure of the 14-membered π perimeter. To this end, these compounds have been investigated by proton magnetic resonance,[2] X-ray crystallography,[3] and photoelectron spectroscopy[4] as well as by optical absorption, polarized fluorescence, and circular dichroism.[5] In particular, two of these studies[4,5] have aimed at assessing the importance of (i) distortions of the π perimeter from planarity, (ii) homoconjugative interaction between the formally nonbonded but spatially proximate bridged centers, (iii) inductive perturbation by the bridging groups, and (iv) hyperconjugation of the perimeter π orbitals with the σ orbitals of these groups. The most sensitive tool to probe the effects of (i)–(iv) on the electronic structure is ESR spectroscopy, since the nodal properties of the singly occupied orbitals enable one to determine the energetic sequence of the frontier MO's and thus to find out how their degeneracies are affected by the introduction of the bridging group.[6a] About 12 years ago, ESR studies of the radical anions of several 1,6:8,13-bridged [14]annulenes established that the singly occupied orbitals in all these species correlate with the perimeter LUMO of the *same* nodal properties.[7] This statement also holds for the radical anions of other bridged [14]annulenes in the series which have since been studied.[8] As is pointed out in the present paper, such a uniform behavior is consistent with the prediction that the perturbations, which are effective in removing the degeneracy of the perimeter LUMO's, should work in the *same* direction. Thus, although the studies of the radical anions of 1,6:8,13-bridged [14]annulenes give insight into the effect of nonplanarity on the proton coupling constants,[7,8] they are less useful for sorting out the role of individual perturbations in removing orbital degeneracy. It is also shown that the situation is more favorable in the case of the corresponding radical cations, since some of the pertur-

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[1] For reviews see: Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237–262. *Ibid.* **1971**, *28*, 355–377. *Ibid.* **1982**, *54*, 1015–1039. *Isr. J. Chem.* **1980**, *20*, 215–224.

[2] Alscher, A.; Bremser, W.; Cremer, D.; Günther, H.; Schmickler, H.; Sturm, W.; Vogel, E. *Chem. Ber.* **1975**, *108*, 640–656.

[3] Simonetta, M. *Pure Appl. Chem.* **1980**, *52*, 1597–1610.

[4] Batich, C.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2288–2306.

[5] Kolc, J.; Michl, J.; Vogel, E. *J. Am. Chem. Soc.* **1976**, *98*, 3935–3948.

[6] See, e.g.: Gerson, F. "High Resolution ESR Spectroscopy"; Verlag Chemie and Wiley: Weinheim and New York, 1970; (a) pp 111–124; (b) pp 74–82; (c) p 42.

[7] Gerson, F.; Müllen, K.; Vogel, E. *J. Am. Chem. Soc.* **1972**, *94*, 2924–2929.

[8] Gerson, F.; Knöbel, J.; Lopez, J.; Vogel, E., unpublished results.

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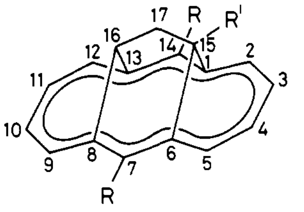
Table I. Proton Coupling Constants (a_{H_μ}) in mT[a] and g Values[b] for the Radical Cations of 1,6:8,13-Propane-1,3-diylidene[14]annulene (**1**) and Its Derivatives **2**, **3**, **4**, and **5** and of 1,6:8,13-Ethanediylidene[14]annulene (**6**) and Its Derivatives **7** and **8**

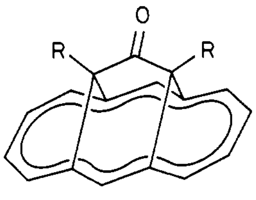
cation	position μ 2,5,9,12	3,4,10,11	7,14	15,16	17	g
$\mathbf{1}^{+\cdot}$	0.325 (4 H)	0.058 (4 H)	0.457 (2 H)	0.140 (2 H)	0.140 (2 H)	2.0022
$\mathbf{2}^{+\cdot}$	0.266 (4 H)	0.058 (4 H)	0.536 (6 H)[c]	0.137 (2 H)	0.137 (2 H)	2.0024
$\mathbf{3}^{+\cdot}$[d]	0.325 (2 H)	0.056 (2 H)	0.400 (2 H)	0.145 (1 H)	0.145 (2 H)	2.0022
	0.295 (2 H)	0.056 (2 H)		0.019 (3 H)[e]		
$\mathbf{4}^{+\cdot}$	0.318 (4 H)	0.038 (4 H)	0.413 (2 H)	0.136 (2 H)		2.0020
$\mathbf{5}^{+\cdot}$	0.301 (4 H)	0.080 (4 H)	0.322 (2 H)	0.021 (6 H)[c]		2.0020
$\mathbf{6}^{+\cdot}$	0.014 (4 H)	0.248 (4 H)	0.092 (2 H)	2.815 (2 H)		2.0027[f]
$\mathbf{7}^{+\cdot}$	0.036 (2 H)	0.257 (2 H)	0.091 (2 H)	2.747 (1 H)		2.0027[f]
	0.013 (2 H)	0.254 (2 H)		0.040 (3 H)[e]		
$\mathbf{8}^{+\cdot}$	0.032 (4 H)	0.257 (4 H)	0.081 (2 H)	0.038 (6 H)[c]		2.0027

[a] Experimental error in the coupling constants for all radical cations, with the exception of $\mathbf{3}^{+\cdot}$, ±1%. [b] Experimental error in g values is ±0.0001 [c] Coupling constant of protons in two methyl substituents. [d] Because of the complexity of the ESR spectrum of $\mathbf{3}^{+\cdot}$ ($3^6 \times 2 \times 4 = 4374$ hyperfine components) the coupling constants for this radical cation are subject to some uncertainty. [e] Coupling constant of protons in one methyl substituent. [f] Corrected for second-order shift.

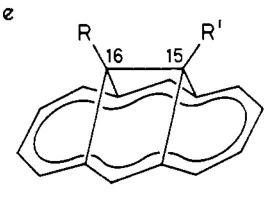
bations (i–iv) are predicted to have *opposite* effects on the energies of the degenerate perimeter HOMO's. As a consequence, the singly occupied orbitals in the radical cations of various 1,6:8,13-bridged [14]annulenes might correlate with perimeter HOMO's of *different* nodal properties, if the relative importance of the individual perturbations would vary on passing from one bridged [14]annulene to another. The ESR studies reported in the present paper demonstrate that this is indeed the case and, thus, they throw light upon the interplay of the perturbations in removing the degeneracy of the perimeter HOMO's. The bridged [14]annulenes of which the radical cations have been dealt with are 1,6:8,13-propane-1,3-diylidene[14]annulene (**1**), 1,6:8,13-propane-1,3-diylidene-7,14-dimethyl[14]annulene (**2**), 1,6:8,13-butane-1,3-diylidene[14]annulene (**3**), 1,6:8,13-(2-oxopropane-1,3-diylidene)[14]annulene (**4**), 1,6:8,13-(3-oxopentane-2,4-diylidene)[14]annulene (**5**), 1,6:8,13-ethanediylidene[14]annulene (**6**), 1,6:8,13-propane-1,2-diylidene[14]annulene (**7**), and 1,6:8,13-butane-2,3-diylidene[14]annulene (**8**).



1 R = R' = H
2 R = Me, R' = H
3 R = H, R' = Me



4 R = H
5 R = Me



6 R = R' = H
7 R = H, R' = Me
8 R = R' = Me

Experimental Section

With the exception of the two recently prepared compounds, **3** and **5**,[9] the syntheses of the 1,6:8,13-bridged [14]annulenes **1**–**8** have been described previously: **1**,[10] **2**,[11] **4**,[10] **6**,[12] **7**,[13] and **8**.[14]

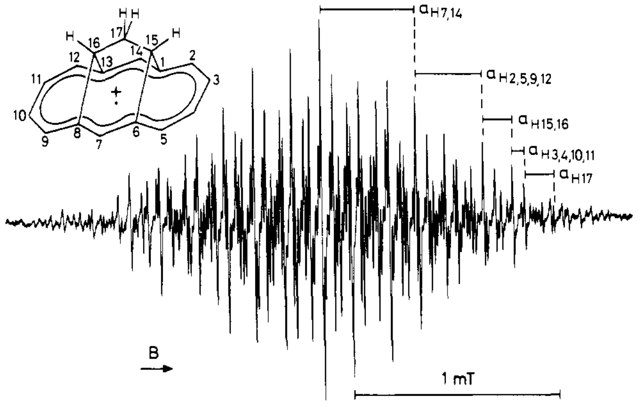


Figure 1. ESR spectrum of the radical cation of 1,6:8,13-propane-1,3-diylidene[14]annulene (**1**). Solvent, CH_2Cl_2; temperature, 213 K.

The radical cations $\mathbf{1}^{+\cdot}$ to $\mathbf{8}^{+\cdot}$ were generated by oxidation of the corresponding neutral compounds with freshly sublimed $AlCl_3$ in methylene chloride. The reactions proceeded rather slowly, in contrast to the rapid oxidation of the structurally related anthracene (**9**) under the same conditions, and the resulting radical cations exhibited lower persistence than $\mathbf{9}^{+\cdot}$. The ESR studies were conducted between 183 and 253 K, in which range the coupling constants did not markedly depend on the temperature. Raising the temperature led, in general, to an improved resolution, but it caused a decrease in the intensity, due to the decay of the radical cations. In the case of $\mathbf{3}^{+\cdot}$, the disappearance of the ESR spectrum was accompanied by the emergence of a signal arising from $\mathbf{9}^{+\cdot}$.[15] Proton ENDOR spectra of low intensity could be observed only for the relatively persistent radical cations $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$; attempts to perform general TRIPLE experiments were unsuccessful. The instrumentation consisted of a Varian-E9-ESR spectrometer and a Varian-ENDOR-1700 system. For the TRIPLE experiments, an ER-252-ENMR system, coupled to an ER-200-E/D-SRC spectrometer, was used at the BRUKER Analytische Messtechnik, Rheinstetten, West Germany.

Results

1,6:8,13-Propane-1,3-diylidene[14]annulene (1) and Derivatives 2, 3, 4, and 5. Figure 1 shows the ESR spectrum of the radical cation $\mathbf{1}^{+\cdot}$. The proton coupling constants derived therefrom are listed in Table I, along with those for the radical cations $\mathbf{2}^{+\cdot}$, $\mathbf{3}^{+\cdot}$, $\mathbf{4}^{+\cdot}$, and $\mathbf{5}^{+\cdot}$. Assignments of the three two-proton coupling constants for $\mathbf{1}^{+\cdot}$ to the α protons[16] in the 7,14-positions ($a_{H7,14}$ = 0.457 mT), the two β protons[16] in the 15,16-positions ($a_{H15,16}$ = 0.140 mT), and the two γ protons[16] in the 17-position (a_{H17}

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[9] Vogel, E., et al., unpublished results.

[10] Vogel, E.; Vogel, A.; Kübbeler, H.-K.; Sturm, W. *Angew. Chem.* **1970**, *82*, 512–513. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 514–515.

[11] Meul, T. Ph.D. Thesis, Köln, 1982; pp 162–189.

[12] Vogel, E.; Reel, H. *J. Am. Chem. Soc.* **1972**, *94*, 4388–4389.

[13] Reel, H. Ph.D. Thesis, Köln, 1972; pp 46–70.

[14] Balci, M. Ph.D. Thesis, Köln, 1976; pp 33–41.

[15] (a) Carrington, A.; Drawnieks, F.; Symons, M. C. R. *J. Chem. Soc.* **1959**, 947–952. (b) Bolton, J. R.; Fraenkel, G. K. *J. Chem. Phys.* **1964**, *40*, 3307–3320.

[16] It is conventional in ESR spectroscopy to denote protons separated from a π center by 0, 1, 2,... sp^3-hybridized carbon atoms as α, β, γ,..., respectively. Thus, the protons directly bound to the carbon centers of the π perimeter (2,3,4,5,7,9,10,11,12,14-positions) are α, while those in the bridging alkanediylidene group are β (15,16-positions) or γ (17-position). Likewise, the protons in the methyl substituents attached to the π perimeter (7,14-positions in **2**) are β.

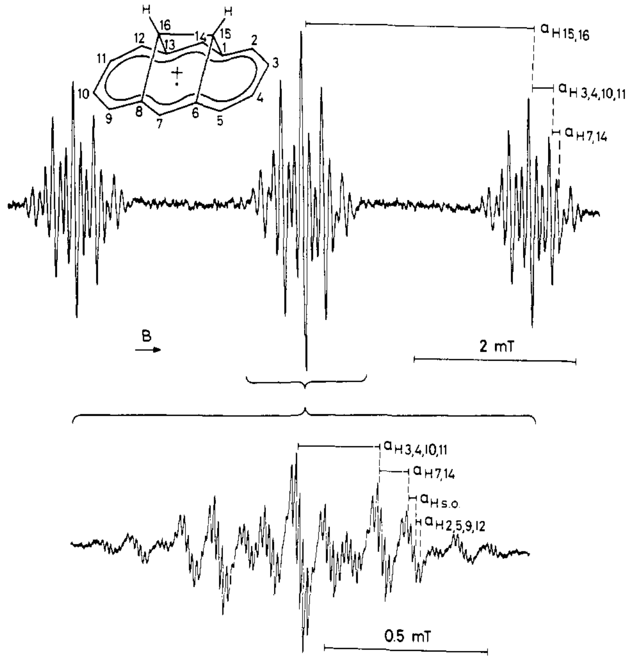

Figure 2. Top: ESR spectrum of the radical cation of 1,6:8,13-ethanediylidene[14]annulene (**6**). Solvent, CH_2Cl_2; temperature, 213 K. Bottom: Central group of lines on an expanded scale. s.o. = second-order splitting.

= 0.140 mT) follow unequivocally from the comparison of the hyperfine data for the five radical cations $1^{+\cdot}$ to $5^{+\cdot}$. In particular, it is essential to note that the largest value (0.457 mT) belongs to the α protons in the 7,14-positions. Assignments of the two four-proton coupling constants to the α protons in the 2,5,9,12- and 3,4,10,11-positions ($a_{H2,5,9,12}$ = 0.325 mT and $a_{H3,4,10,11}$ = 0.058 mT) are justified by an MO model presented in the Discussion section. A strong experimental support for these assignments is provided by comparing the hyperfine data for $1^{+\cdot}$ and $2^{+\cdot}$ with those of the radical cations of anthracene (**9**)[15b] and its 9,10-dimethyl derivative (**10**).[17]

The 7,14-dimethyl substitution of $1^{+\cdot}$, to yield $2^{+\cdot}$, leads to the replacement of the coupling constant ($a_{H7,14}$ = 0.457 mT) of the two α protons in these positions by that (0.536 mT) of the six β protons[16] in the two methyl groups. The ratio 0.457 mT/0.536 mT = 0.85 is very close to the ratio 0.653 mT/0.800 mT = 0.82 for the coupling constants of the two α protons in the corresponding 9,10-positions of $9^{+\cdot}$ and of the six β protons in the two methyl groups of $10^{+\cdot}$. A relationship of the same kind holds for the coupling constants of the four α protons in the 2,5,9,12-positions of $1^{+\cdot}$ and $2^{+\cdot}$ and of those in the corresponding 1,4,5,8-positions of $9^{+\cdot}$ and $10^{+\cdot}$, if the values 0.325 and 0.266 mT are assigned to the protons in the pertinent positions of $1^{+\cdot}$ and $2^{+\cdot}$, respectively. The ratio 0.325 mT/0.266 mT = 1.22 for $1^{+\cdot}/2^{+\cdot}$ is then almost equal to the analogous number 0.306 mT/0.254 mT = 1.20 for $9^{+\cdot}/10^{+\cdot}$.

1,6:8,13-Ethanediylidene[14]annulene (6) and Derivatives 7 and 8. An ESR spectrum, which strikingly differs from that of $1^{+\cdot}$ (Figure 1), is observed for the radical cation $6^{+\cdot}$. As is evident from Figure 2 (top), in which this spectrum is reproduced, its most prominent hyperfine feature is the splitting into three widely separated groups of lines. The very large coupling constant (2.815 mT) responsible for this splitting must be due to the two equivalent β protons in the 15,16-positions, since values of such a magnitude are precluded for α protons in a π radical extending over 14 centers. This assignment ($a_{H15,16}$ = 2.815 mT) is confirmed by the ESR spectra of the radical cations $7^{+\cdot}$ and $8^{+\cdot}$, in which successive replacement of the 15,16-hydrogen atoms by methyl substituents reduces the number of groups of lines from three to two and one, respectively. Figure 2 (bottom) displays the central group of lines in the ESR spectrum of $6^{+\cdot}$, taken on an expanded scale. The improved resolution enables one not only to determine the smallest coupling constant, due to four α protons, but also to observe the second-order splitting[18a] (0.025 mT) associated with the β-proton coupling constant ($a_{H15,16}$).

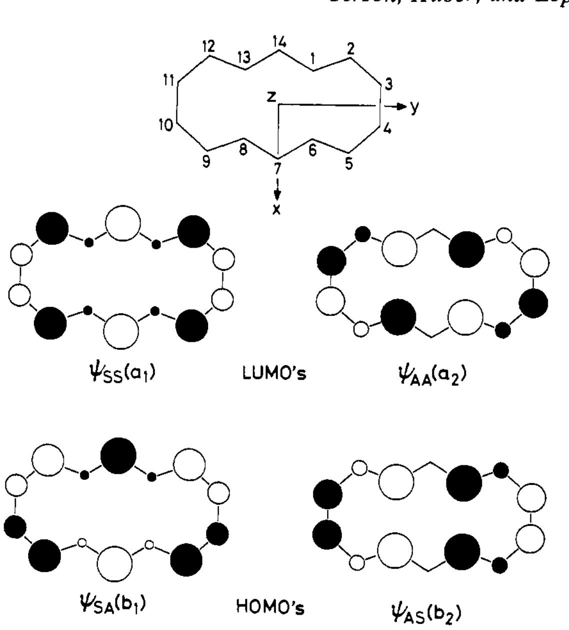

Figure 3. Schematic representation of the frontier orbitals of the 14-membered π perimeter. The areas of the circles are proportional to the squares of the LCAO coefficients. Full and blank circles symbolize opposite signs of these coefficients.

The hyperfine data for the radical cations $6^{+\cdot}$, $7^{+\cdot}$, and $8^{+\cdot}$ are given in Table I, adjoined to those for $1^{+\cdot}$ to $5^{+\cdot}$. Assignment of the second two-proton coupling constant to the α protons in the 7,14-positions of $6^{+\cdot}$ is straightforward. It is noteworthy that this value ($a_{H7,14}$ = 0.092 mT) is relatively small. The two four-proton coupling constants are assigned to the α protons in the 2,5,9,12- and 3,4,10,11-positions ($a_{H2,5,9,12}$ = 0.014 mT and $a_{H3,4,10,11}$ = 0.248 mT) with the aid of an MO model discussed below.

The g values for $6^{+\cdot}$, $7^{+\cdot}$, and $8^{+\cdot}$ are throughout larger than those for $1^{+\cdot}$ to $5^{+\cdot}$ (Table I).

Discussion

MO Model: π Perimeter Frontier Orbitals and Removal of Their Degeneracies by the Bridging Groups. A convenient starting point for the interpretation of the experimental results is the MO model of the 14-membered π perimeter. For the orbitals of an ideal perimeter of the symmetry D_{14h}, the LCAO coefficients of the $2p_z$ AO's, ϕ_μ, at the centers μ = 1–14 are totally determined by this point group. Both the LUMO's

$$\psi_{SS}(a_1) = 0.084(\phi_1 + \phi_6 + \phi_8 + \phi_{13}) + 0.341(\phi_2 + \phi_5 + \phi_9 + \phi_{12}) - 0.236(\phi_3 + \phi_4 + \phi_{10} + \phi_{11}) - 0.378(\phi_7 + \phi_{14})$$

$$\psi_{AA}(a_2) = 0.368(\phi_1 - \phi_6 + \phi_8 - \phi_{13}) - 0.164(\phi_2 - \phi_5 + \phi_9 - \phi_{12}) - 0.296(\phi_3 - \phi_4 + \phi_{10} - \phi_{11})$$

and the HOMO's

$$\psi_{SA}(b_1) = 0.084(\phi_1 - \phi_6 - \phi_8 + \phi_{13}) - 0.341(\phi_2 - \phi_5 - \phi_9 + \phi_{12}) - 0.236(\phi_3 - \phi_4 - \phi_{10} + \phi_{11}) - 0.378(\phi_7 - \phi_{14})$$

$$\psi_{AS}(b_2) = 0.368(\phi_1 + \phi_6 - \phi_8 - \phi_{13}) + 0.164(\phi_2 + \phi_5 - \phi_9 - \phi_{12}) - 0.296(\phi_3 + \phi_4 - \phi_{10} - \phi_{11})$$

depicted in Figure 3, are doubly degenerate. In order to facilitate the discussion, the numbering of the $2p_z$ AO's, ϕ_μ, at the π centers, μ, corresponds to that of the positions in 1,6:8,13-bridged [14]-annulenes. For the same reason, the shape of the perimeter has

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[17] Bolton, J. R.; Carrington, A.; McLachlan, A. D. *Mol. Phys.* **1962**, 5, 31–41.

[18] See, e.g.: Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance: Elementary Theory and Practital Applications"; McGraw-Hill, New York, 1972; (a) pp 77–79; (b) pp 99–105.

been adapted to the carbon framework of the cyclic π system in these compounds. (As is argued further on, the energies of the MO's are not greatly affected by such a deformation.) The classification of the MO's as S (symmetric) and A (antisymmetric) characterizes the behavior with respect to the mirror planes *xz* (first subscript) and *yz* (second subscript). The alternative labels a_1, a_2, b_1, and b_2 refer to irreducible representations of the point group C_{2v} which strictly applies to **1**, **2**, **4**, **5**, **6**, and **8**, and approximately to **3** and **7**.

An effect of bridging the perimeter is to remove the degeneracies of the frontier orbitals. As stated in the introduction, it is usual to discuss such an effect in terms of various perturbations.[4,5,19] Conveniently, one can first exclude the transannular interactions and the electronic perturbations by the bridging group, so that solely the lowering of the perimeter symmetry from D_{14h} to C_{2v} is considered. Moreover, this symmetry lowering may be regarded as being brought about in two stages, an *in-plane deformation* from D_{14h} to D_{2h} followed by an *out-of-plane distortion* from D_{2h} to C_{2v}.

In-Plane Deformation. Calculations of the PPP type indicate that the π orbitals of a hypothetical planar [14]annulene with an anthracene-like perimeter of D_{2h} symmetry are almost identical with those of an ideal 14-membered perimeter of D_{14h} symmetry.[5] Deformation of the perimeter from D_{14h} to D_{2h} should thus have a negligible effect on the energies of the degenerate frontier orbitals.

Out-of-Plane Distortions. Although transformation of a planar perimeter of D_{2h} symmetry into a nonplanar one of C_{2v} symmetry influences the absolute values of the α-proton coupling constants,[7,20] its effect on the energies of the perimeter frontier orbitals is expected to be only a minor one. This statement is supported by a first-order perturbation treatment, in which the π bonding has been modified by twisting the $2p_z$ axes at the consecutive centers;[4] the twist angles were those determined by the X-ray crystallographic analyses of the 1,6:8,13-bridged [14]annulenes.[3] According to this treatment, the nonplanarity should slightly lower the energies of *both* LUMO's, ψ_{SS} and ψ_{AA}, while *both* HOMO's, ψ_{SA} and ψ_{AS}, should correspondingly be slightly destabilized. The actual effect must be even smaller than the calculated one, since the $2p_z$ axes[21] need not accommodate themselves to the twist angles but can orient themselves in such a way as to minimize the losses in the π delocalization energy.[4,22]

In conclusion, not only an *in-plane deformation* from D_{14h} to D_{2h} but also an *out-of-plane distortion* from D_{2h} to C_{2v} is predicted to be rather ineffective in removing the degeneracies of the frontier orbitals. Consequently, the following discussion will be restricted to transannular interactions, which are generally called *homoconjugation*, as well as to perturbations by the bridging group, which are usually dissected into *inductive* and *hyperconjugative contributions*. Relevant in this respect are the LCAO coefficients $c_{SS,\mu}$, $c_{AA,\mu}$, $c_{SA,\mu}$, and $c_{AS,\mu}$ at the bridged centers μ = 1, 6, 8, and 13 for the MO's ψ_{SS}, ψ_{AA}, ψ_{SA}, and ψ_{AS}. Since such coefficients are very small in magnitude for ψ_{SS} and ψ_{SA} ($|c_{SS,\mu}| = |c_{SA,\mu}| = 0.084$) and rather large for ψ_{AA} and ψ_{AS} ($|c_{AA,\mu}| = |c_{AS,\mu}| = 0.368$), the energies of the two former MO's will be only marginally affected relative to those of the two latter ones. It is therefore reasonable to restrict the considerations to the LUMO ψ_{AA} and the HOMO ψ_{AS}.

Homoconjugation. Overlaps of the $2p_z$ AO's, ϕ_μ, at the two pairs of formally nonbonded but spatially proximate bridged centers, μ, 1 with 6 and 8 with 13, lead to through-space transannular interactions[23] (homoconjugation) which depend on the orientation and the distance of the interacting AO's. In the first-order perturbation treatment, the extent of these interactions is proportional to the products of the LCAO coefficients at the pertinent bridged centers. Due to the different nodal properties of the LUMO ψ_{AA} and the HOMO ψ_{AS}, the products $c_{AA,1}c_{AA,6} = c_{AA,8}c_{AA,13}$ are negative, while $c_{AS,1}c_{AS,6} = c_{AS,8}c_{AS,13}$ have a positive sign. The MO's ψ_{AA} and ψ_{AS} will thus be destabilized and stabilized, respectively, to an equal extent, so that the predicted energy sequence is ψ_{AA} above ψ_{SS} and ψ_{AS} below ψ_{SA}.

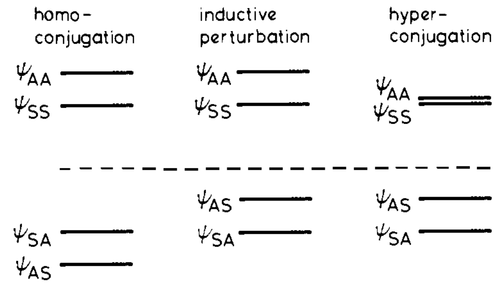

Figure 4. Removal of the degeneracies of the frontier perimeter orbitals in the 1,6:8,13-bridged [14]annulenes by the "individual" effects of homoconjugative, inductive, and hyperconjugative perturbations (not to scale).

Inductive Perturbation. The existence of the so-called "inductive effect" of the alkyl substituents on π systems, i.e., the behavior of such substituents as electron-releasing groups, has been disputed in the last few years, on grounds of electron-transmission studies in the gas phase[24] and of ab initio calculations.[25] Nevertheless, the heuristic value of such an "effect" in rationalizing the experimental findings in solution is well established.[6a,18b,26] For instance, it has recently been concluded that a destabilization of the perimeter frontier orbitals by electron-releasing alkyl substituents is hardly to be passed by in interpreting the ESR spectra of derivatives of the cyclopentadienyl radical.[27] Since such a destabilization is, in the first-order perturbation treatment, proportional to the squares ($c_{AA,\mu}{}^2$ and $c_{SA,\mu}{}^2$) of the LCAO coefficients at the bridged centers, μ, it will equally raise the energies of the LUMO ψ_{AA} and the HOMO ψ_{AS}. The sequence predicted as a result of the inductive destabilization is thus ψ_{AA} above ψ_{SS} and ψ_{AS} above ψ_{SA}.

Hyperconjugation. Of the two frontier orbitals under consideration (the LUMO ψ_{AA} and the HOMO ψ_{AS}), the former exhibits a nodal plane (*yz*) through the bridging carbon atoms in the 15,16-positions and its energy will not be affected by hyperconjugation. On the other hand, ψ_{AS} can interact with an alkanediylidene σ orbital belonging to the same irreducible representation (b_2). This interaction will raise the energy of ψ_{AS} so that the predicted sequence is ψ_{AS} above ψ_{SA} (with ψ_{SS} and ψ_{AA} remaining almost degenerate).

Figure 4 summarizes the expected "individual" effects of the *homoconjugative*, *inductive*, and *hyperconjugative perturbations* on the energetic sequence of the frontier orbitals. For the LUMO's, the statement is straightforward. In the absence of a significant effect of hyperconjugation, the degeneracy of ψ_{SS} and ψ_{AA} is removed by homoconjugative and inductive perturbations; both place ψ_{AA} above ψ_{SS}. Thus, in the radical anions of 1,6:8,13-briged [14]annulenes, the singly occupied orbitals should throughout be ψ_{SS}-like. The statement is less unequivocal for the HOMO's. In this case, the effect of homoconjugation, which lowers the energy of ψ_{AS} with respect to ψ_{SA}, is opposite to that of the inductive and hyperconjugative perturbations which shift ψ_{AS} above ψ_{SA}. Clearly, such a situation is interesting, since the actual energetic sequence of the HOMO's may depend on the

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[21] The notation $2p_z$ for the AO's (ϕ_μ) at the centers (μ) in the 14-membered perimeter is used for convenience, despite the fact that the axes of these AO's in the 1,6:8,13-bridged [14]annulenes deviate from the *z* direction of the twofold symmetry axis.

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Table II. π-Spin Populations $\rho_\mu^{SS} = \rho_\mu^{SA}$ and $\rho_\mu^{AA} = \rho_\mu^{AS}$ Calculated for the Single Occupancy of the Perimeter Frontier Orbitals ψ_{SS}, ψ_{SA}, ψ_{AA}, and ψ_{AS}: Comparison of the Predicted α-Proton Coupling Constants ($a_{H_\mu}{}^{SS}$, $a_{H_\mu}{}^{AA}$, $a_{H_\mu}{}^{SA}$, and $a_{H_\mu}{}^{AS}$) with the Experimental Data (a_{H_μ}) for the Radical Anions and the Radical Cations of 1,6:8,13-Propane-1,3-diylidene- (**1**) and 1,6:8,13-Ethanediylidene[14]annulene (**6**)[a]

	center μ			
	1,6,8,13	2,5,9,12	3,4,10,11	7,14
$\rho_\mu^{SS} = \rho_\mu^{SA}$	−0.045	+0.152	+0.043	+0.200
$\rho_\mu^{AA} = \rho_\mu^{AS}$	+0.187	−0.008	+0.100	−0.058
$a_{H_\mu}{}^{SS}$		−0.350	−0.099	−0.460
$a_{H_\mu}{}^{AA}$		+0.018	−0.230	+0.133
a_{H_μ} ($\mathbf{1}^{-}\cdot$)[b]		0.280	0.010	0.341
a_{H_μ} ($\mathbf{6}^{-}\cdot$)		0.323	0.040	0.446
$a_{H_\mu}{}^{SA}$		−0.395	−0.112	−0.520
$a_{H_\mu}{}^{AS}$		+0.021	−0.260	+0.151
a_{H_μ} ($\mathbf{1}^{+}\cdot$)		0.325	0.058	0.457
a_{H_μ} ($\mathbf{6}^{+}\cdot$)		0.014	0.248	0.092

[a] All coupling constants in mT. [b] Due to better resolution of the ESR spectrum, these values are slightly more precise than those reported previously.[7]

relative importance of these perturbations which can differ for [14]annulenes bridged by different groups. As a consequence, the singly occupied orbital in the radical cations would change its nodal properties on passing from one 1,6:8,13-bridged [14]-annulene to another.

Comparison with Experiment. Table II lists the π-spin populations $\rho_\mu^{SS} = \rho_\mu^{SA}$ and $\rho_\mu^{AA} = \rho_\mu^{AS}$ calculated by the McLachlan procedure[28] ($\lambda = 1.2$) for the carbon centers (μ) and the single occupancy of the MO's ψ_{SS}, ψ_{SA}, ψ_{AA}, and ψ_{AS} in the radical ions of a hypothetical planar 14-membered perimeter. For a direct comparison with the experimental data, the π-spin populations at those centers (μ) which bear hydrogen atoms in 1,6:8,13-bridged [14]annulenes have been converted into α-proton coupling constants a_{H_μ} with the use of the McConnell equation[29]

$$a_{H_\mu}{}^{SS} = Q\rho_\mu^{SS} \quad a_{H_\mu}{}^{AA} = Q\rho_\mu^{AA} \quad \text{(radical anions)}$$

$$a_{H_\mu}{}^{SA} = Q\rho_\mu^{SA} \quad a_{H_\mu}{}^{AS} = Q\rho_\mu^{AS} \quad \text{(radical cations)}$$

The value of the proportionality factor Q was taken as −2.3 mT for the radical anions and −2.6 mT for the radical cations, since the coupling constants a_{H_μ} are usually larger in positively charged π radicals than in negatively charged ones.[6b]

The calculated coupling constants $a_{H_\mu}{}^{SS}$, $a_{H_\mu}{}^{AA}$, $a_{H_\mu}{}^{SA}$, and $a_{H_\mu}{}^{AS}$ are compared in Table II with their experimental counterparts for the radical ions of 1,6:8,13-propane-1,3-diylidene (**1**)[7] and 1,6:8,13-ethanediylidene[14]annulene (**6**).[8] The observed α-proton coupling constants for both radical anions $\mathbf{1}^{-}\cdot$ and $\mathbf{6}^{-}\cdot$ resemble $a_{H_\mu}{}^{SS}$ and thus point to a single occupancy of a ψ_{SS}-like orbital. This finding, which is general for the radical anions of all 1,6:8,13-bridged [14]annulenes investigated so far,[7,8] is in accord with the prediction of the MO model (Figure 4). As discussed in more breadth in a previous paper,[7] the fact that the observed α-proton coupling constants are smaller than the corresponding $|a_{H_\mu}{}^{SS}|$ values is due to the distortions of the 14-membered π perimeter from planarity and the resulting slight "σ admixture" to the π MO's. (Since the distortions become less pronounced on passing from $\mathbf{1}^{-}\cdot$ to $\mathbf{6}^{-}\cdot$,[3] the experimental data for $\mathbf{6}^{-}\cdot$ are closer to $a_{H_\mu}{}^{SS}$ than those for $\mathbf{1}^{-}\cdot$.)

In contrast to $\mathbf{1}^{-}\cdot$ and $\mathbf{6}^{-}\cdot$, the α-proton coupling constants for the corresponding radical cations do not resemble the same set of calculated values. Whereas the experimental data for $\mathbf{1}^{+}\cdot$ compare favorably with $|a_{H_\mu}{}^{SA}|$, those for $\mathbf{6}^{+}\cdot$ are clearly compatible with $|a_{H_\mu}{}^{AS}|$. Of highest diagnostic value is, in this respect, the two-proton coupling constant $a_{H7,14}$ which for both radical cations has been assigned on experimental grounds, whereas assignments of the two four-proton coupling constants $a_{H2,5,9,12}$ and $a_{H3,4,10,11}$ rely partially ($\mathbf{1}^{+}\cdot$) or entirely ($\mathbf{6}^{+}\cdot$) on correlation with their calculated counterparts. (As in the case of the corresponding radical anions, distortions of the perimeter from planarity are responsible for the finding that the coupling constants of the α protons in $\mathbf{1}^{+}\cdot$ and $\mathbf{6}^{+}\cdot$ are throughout smaller than $|a_{H_\mu}{}^{SA}|$ and $|a_{H_\mu}{}^{AS}|$, respectively.)

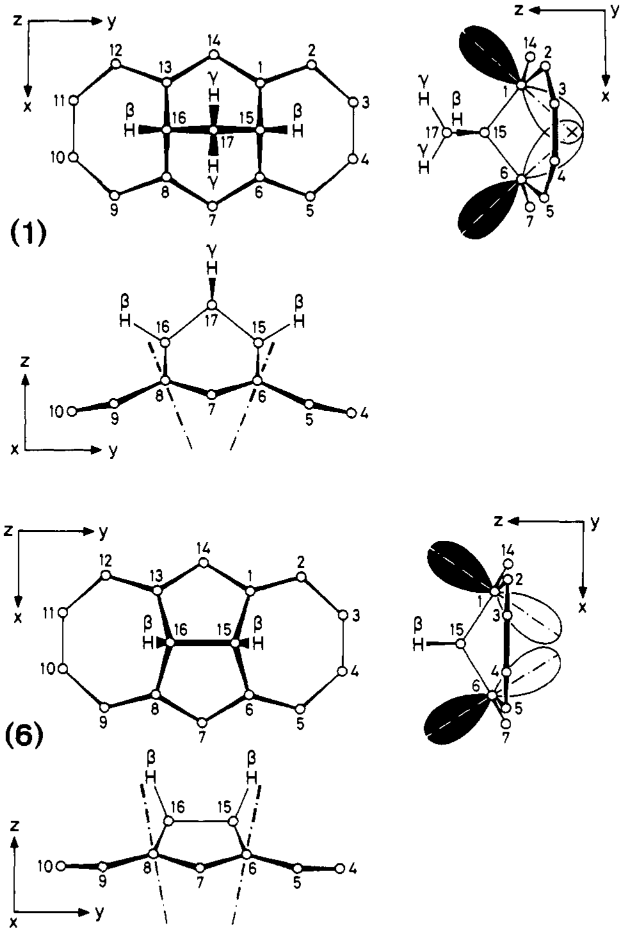

Figure 5. Projections of the carbon frameworks of 1,6:8,13-propane-1,3-diylidene- (**1**) and 1,6:8,13-ethanediylidene[14]annulene (**6**) on *xy*, *xz*, and *yz* planes. The —·— lines indicate the presumed directions of the $2p_z$ axes[21] at the bridged carbon centers.

Thus, *on going from* $\mathbf{1}^{+}\cdot$ *to* $\mathbf{6}^{+}\cdot$, *there is a change in the nodal properties of the singly occupied orbital which must be considered as being* ψ_{SA}*-like in* $\mathbf{1}^{+}\cdot$ *and* ψ_{AS}*-like in* $\mathbf{6}^{+}\cdot$. This change indicates a "switch" in the energetic sequence of the two perimeter HOMO's, due to the delicate balance of the homoconjugative, inductive, and hyperconjugative perturbations (Figure 4). In particular, homoconjugation and hyperconjugation are expected to be sensitive to the nature of the alkanediylidene bridging group, whereas the effect of the inductive perturbation should be less dependent on such a group.

Interpretation. Figure 5 illustrates the geometries of **1** and **6** by projecting the carbon frameworks on the planes *xy*, *xz*, and *yz*. The locations of the carbon atoms are those indicated by molecular models and determined by the X-ray crystallographic structure analyses of **1**[30] and **8**,[31] the 15,16-dimethyl derivative of **6**. On going from **1** to **6**, the 14-membered π perimeter is flattened and the through-space overlaps between the two pairs of the $2p_z$ AO's(ϕ_μ)[21] at the bridged centers (μ), 1 with 6 and 8 with 13, are reduced (cf. *xz* projections). As a result, the homoconjugative interactions, which lower the energy of ψ_{AS} relative

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to ψ_{SA}, are decreased. A further consequence of replacing the propane-1,3-diylidene (**1**) by the ethanediylidene bridging group (**6**) is an almost perfect alignment of the C15–Hβ and C16–Hβ bonds with the $2p_z$ axes at the adjacent bridged centers (cf. *yz* projection). The hyperconjugative interaction of ψ_{AS} with a σ orbital of the bridging group is thus enhanced, leading to an increased destabilization of this perimeter HOMO relative to ψ_{SA}.

The "orbital switch" on passing from **1** to **6** can accordingly be rationalized as follows (Figure 4). *In **1**, the effect of homoconjugation overrides that of inductive and hyperconjugative perturbations*, so that ψ_{AS} is lowered in energy relative to ψ_{SA}. It is therefore a ψ_{SA}-like orbital which is singly occupied in $\mathbf{1}^{+\cdot}$. On the other hand, owing to a weaker homoconjugation and a stronger hyperconjugation, *the effect of inductive and hyperconjugative perturbations is dominant in **6***. As a consequence, ψ_{AS} is raised in energy above ψ_{SA}, and the singly occupied orbital in $\mathbf{6}^{+\cdot}$ is ψ_{AS}-like.

The very large coupling constant ($a_{H15,16} = 2.815$ mT) of the two β protons in the 15,16-positions of $\mathbf{6}^{+\cdot}$ is perfectly in line with the single occupancy of an ψ_{AS}-like orbital and a strong hyperconjugative interaction between ψ_{AS} and a σ orbital of the bridging ethanediylidene group. Since each of the β-proton-bearing carbon atoms (15 and 16) is linked to two bridged centers (μ and μ'), the appropriate relationship is[32]

$$a_{H15,16} = B(c_{AS,\mu} + c_{AS,\mu'})^2 \cos^2 \theta$$

where $c_{AS,\mu}$ and $c_{AS,\mu'}$ are the pertinent LCAO coefficients and θ stands for the dihedral angle between the C15–Hβ or C16–Hβ bonds and the $2p_z$ axes at μ and μ'. In $\mathbf{6}^{+\cdot}$, $\mu = 1$ and $\mu' = 6$ for C15–Hβ (i.e., Hβ is H15) and $\mu = 8$ and $\mu' = 13$ for C16–Hβ (i.e., Hβ is H16); moreover, $c_{AS,1} = c_{AS,6} = 0.368$ and $c_{AS,8} = c_{AS,13} = -0.368$. Taking the proportionality factor B as +5 to +6 mT,[33] and θ as 10° (Figure 5, *yz* projection for **6**), one obtains $a_{H15,16} = +2.6$ to $+3.2$ mT, in good agreement with the observed value of 2.815 mT.

The prerequisites for the large coupling constant of the β protons in $\mathbf{6}^{+\cdot}$ are thus (i) the single occupancy of an orbital exhibiting at the bridged centers μ and μ' large coefficients of the same sign and (ii) a far-reaching alignment of C15–Hβ and C16–Hβ bonds with the $2p_z$ axes at μ and μ'.[34] Such prerequisites are missing in $\mathbf{1}^{+\cdot}$. In particular, the nodal properties of the singly occupied orbital preclude a hyperconjugative interaction between this ψ_{SA}-like MO and a σ orbital of the propanediylidene bridging group (the relevant coefficients have opposite signs: $c_{SA,1} = -c_{SA,6}$ and $c_{SA,8} = -c_{SA,13}$). Accordingly, the coupling constant of the two β protons in the 15,16-positions of $\mathbf{1}^{+\cdot}$ is relatively small ($a_{H15,16} = 0.140$ mT) and must be due to another mechanism of spin transfer, presumably to spin polarization. It is interesting to note that the coupling constant of the two γ protons in the 17-position of $\mathbf{1}^{+\cdot}$ has (within the limits of experimental error) the same value as $a_{H15,16}$. This value ($a_{H17} = 0.140$ mT) is rather large for γ protons, since such protons generally give rise to coupling constants which are by 1 order of magnitude smaller than those of β protons.[6c] Closer examination of the geometry of **1** (cf. *xz* projection in Figure 5) indicates that the C17–Hγ bonds are in almost planar W arrangement with the $2p_z$ axes at the bridged centers. Such an arrangement leads to appreciable γ-proton coupling constants when C–Hγ bonds lie in an antinode of the singly occupied orbital,[36] as this is the case for the HOMO ψ_{SA} in $\mathbf{1}^{+\cdot}$.

Concluding Remark. The important aspect of the present work is the striking effect of a relatively slight structural change on the energetic sequence of the frontier orbitals. It is gratifying that this effect can be rationalized in terms of a simple MO model of a π perimeter which is perturbed by the introduction of the bridging group.

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Registry No. **1**, 25835-57-8; **2**, 91491-85-9; **3**, 91491-86-0; **4**, 31575-22-1; **5**, 91491-87-1; **6**, 38765-94-5; **7**, 91491-88-2; **8**, 55647-83-1.

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Exchange Interactions in Bis(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy)copper(II): A Nitroxyl Radical Complex of Copper(II)

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Abstract: The single-crystal EPR spectra and the temperature dependence of the magnetic susceptibility of bis(hexafluoroacetylacetonato)(4-hydroxy-2,2,6,6-tetramethylpiperidinyl-*N*-oxy)copper(II) (Cu(hfac)$_2$(TEMPOL)) have been measured. The compound has a linear chain structure, with a TEMPOL ligand bridging two Cu(hfac)$_2$ moieties, but the EPR spectra are typical of a triplet state, showing that magnetically the compound is a chain of weakly coupled metal–radical pairs. The magnetic coupling between the two spins is ferromagnetic, with a singlet–triplet separation of -13 ± 5 cm^{-1}. The single-crystal EPR spectra show that **g** and **D** are practically parallel to each other. The principal values are the following: $g_x = 2.057$, $g_y = 2.013$, $g_z = 2.157$, $D_x = 88 \times 10^{-4}$ cm^{-1}, $D_y = -1140 \times 10^{-4}$ cm^{-1}, $D_z = 1052 \times 10^{-4}$ cm^{-1}, with z roughly parallel to the Cu–O(TEMPOL) bond direction. The **g** tensor has been decomposed into the copper and radical contributions, yielding information on the nature of the magnetic orbital localized on copper. The zero-field splitting tensor has been decomposed into the sum of a dipolar and an exchange component.

Nitroxyl radicals are widely used as spin probes in biological systems,[1-6] but they are now actively studied also as ligands toward transition-metal ions.[7-10] We found particularly interesting those compound where a Lewis acid/base interaction is present between

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