

## Experimental Section

All of the amines used in these studies were commercially available from Eastman Kodak Co. and Aldrich Chemical Co. They were refluxed briefly over sodium metal (caution, hydrogen gas is generated in this step) and introduced into a high vacuum system<sup>16</sup> where they were condensed into a vessel containing liquid NaK alloy. It was necessary to leave the amines in these vessels from 1 to 3 days and it was found to be imperative that the hydrogen pressure be relieved periodically. Pmr samples were prepared by condensing the amine and internal standard into the sample tube. If dimethylzinc was added to the amine it was added at this point.

(16) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

The amount of dimethylzinc added to each sample was less than  $10^{-5}$  mol as measured *via* a calibrated volume on the vacuum line. All pmr samples were sealed under vacuum to exclude the laboratory atmosphere.

Dimethylzinc was prepared by the method of Hota and Willis<sup>17</sup> using methyl iodide, zinc dust, and copper powder.

Pmr spectra were measured on a Varian A-60-A spectrometer. All pmr parameters were measured by linear interpolation between audiofrequency side bands of TMS and are accurate to  $\pm 0.05$  Hz.

**Acknowledgment.** We would like to thank the Research Corporation for its gracious support of this work.

(17) N. K. Hota and C. J. Willis, *J. Organometal. Chem.*, **9**, 171 (1967).

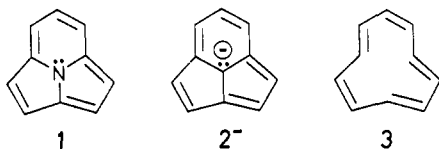
## Electron Spin Resonance Study of Cycl[3.3.3]azine<sup>1</sup> Radical Ions

F. Gerson,\*<sup>2a</sup> Joanna Jachimowicz,<sup>2a</sup> and D. Leaver<sup>2b</sup>

Contribution from *Physikalisch-Chemisches Institut der Universität Basel, 4056 Basel, Switzerland, and the Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland. Received April 27, 1973*

**Abstract:** ESR data ( $g$  values and proton, <sup>14</sup>N, and <sup>13</sup>C coupling constants) are reported for the radical cation and anion of cycl[3.3.3]azine (**4**). A simple model, which correlates the HOMO and LUMO of **4** with the degenerate nonbonding orbitals ( $\psi_S$  and  $\psi_A$ ) of [12]annulene (**6**), accounts for the main features of the  $\pi$ -spin distribution in the radical ions **4**<sup>•+</sup> and **4**<sup>•-</sup>. This model also predicts the almost identical  $\pi$ -spin populations observed for the cation **4**<sup>•+</sup> and the isoelectronic phenalenyl radical (**5**<sup>•-</sup>). The central nitrogen atom in **4**<sup>•+</sup> and **4**<sup>•-</sup> is presumably coplanar with the 12-membered ring. Contrary to the neutral compound **4**, this ring has been considered not to exhibit bond alternation in **4**<sup>•+</sup> and **4**<sup>•-</sup>. In addition to **4**<sup>•+</sup> and **4**<sup>•-</sup>, radical ions of some substituted cycl[3.3.3]azines have been studied by ESR spectroscopy. They include the 1,3-dicyano derivative (**4a**), the 1,3-di-*tert*-butyl ester (**4b**), and the corresponding monoester (**4c**), an intermediate in the thermal decarboxylation of **4b** to **4**. The effect of substitution on the  $\pi$ -spin distributions in the radical ions **4**<sup>•+</sup> and **4**<sup>•-</sup> is qualitatively discussed.

The cyclazines are a class of compounds consisting of a cyclic  $\pi$ -electron system ( $\pi$  perimeter) bridged by a central  $sp^2$ -hybridized nitrogen atom.<sup>3,4</sup> Its first representative, the cycl[3.2.2]azine (**1**),<sup>1</sup> synthe-



sized by Windgassen, *et al.*,<sup>3</sup> can be regarded either as an isoelectronic aza analog of the aceindylenyl anion (**2**<sup>-</sup>) or as a bridged [10]annulene (**3**). In fact, some of the properties of **1** can be rationalized in terms of **2**<sup>-</sup>, whereas others are more satisfactorily accommodated by **3**.<sup>5,6</sup>

(1) According to IUPAC nomenclature, cycl[3.3.3]azine (**4**) must be denoted pyrido[2,1,6-*del*]quinolizine. Analogously, cycl[3.2.2]azine (**1**) and cyclopenta[*h*]cycl[4.2.2]azine (**7**) should be pyrido[2,1,6-*cd*]pyrrolizine and cyclopenta[4,5]azepino[2,1,7-*cd*]pyrrolizine, respectively. For the sake of simplicity and because of the popularity of the cyclazine notation, we have used it throughout the paper.

(2) (a) Universität Basel; (b) University of Edinburgh.

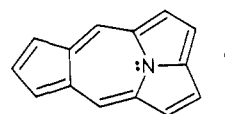
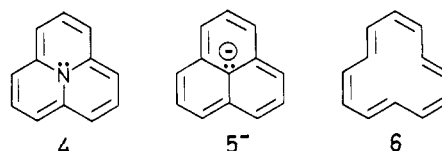
(3) R. J. Windgassen, Jr., W. H. Saunders, Jr., and V. Boekelheide, *J. Amer. Chem. Soc.*, **81**, 1459 (1959).

(4) R. D. Brown and B. A. Collier, *Mol. Phys.*, **2**, 158 (1959).

(5) F. Gerson, E. Heilbronner, N. Joop, and M. Zimmermann, *Helv. Chim. Acta*, **46**, 1940 (1963); V. Boekelheide, F. Gerson, E. Heilbronner, and D. Meuche, *ibid.*, **46**, 1951 (1963).

(6) N. M. Atherton, F. Gerson, and J. N. Murrell, *Mol. Phys.*, **6**, 265 (1963); F. Gerson and J. D. W. van Voorst, *Helv. Chim. Acta*, **46**, 2257 (1963); see also F. Gerson and J. H. Hammons in "Non-benzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, pp 137-140.

Recently, further compounds in the cyclazine series have become available through the work of Leaver, *et al.*,<sup>7,8</sup> who synthesized two novel systems, cycl[3.3.3]azine (**4**) and cyclopenta[*h*]cycl[4.2.2]azine (**7**).<sup>1</sup> The



highly symmetrical compound **4** is of special interest,<sup>9</sup> being structurally related to the isoelectronic phenalenyl anion (**5**<sup>-</sup>) and the [12]annulene (**6**).

The radical anion **1**<sup>•-</sup> of cycl[3.2.2]azine has been extensively studied by ESR spectroscopy.<sup>6</sup> Furthermore, ESR spectra have been recently reported<sup>10</sup> for the radical anions of **7** and some derivatives of **1**. Attempts to prepare the radical cations of **1** and **7** were unsuccessful.<sup>11</sup>

(7) D. Farquhar and D. Leaver, *Chem. Commun.*, 24 (1969).

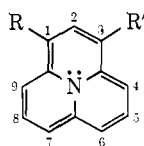
(8) M. A. Jessep and D. Leaver, *ibid.*, 790 (1970).

(9) M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. A*, 1754 (1969).

(10) F. Gerson, J. Jachimowicz, B. Kowert, and D. Leaver, *Helv. Chim. Acta*, **56**, 258 (1973).

(11) F. Gerson and J. Jachimowicz, unpublished work.

Since the highest occupied orbital of cycl[3.3.3]azine (**4**) is predicted to be nonbonding (see Discussion), the ionization potential of **4** should be low,<sup>10</sup> and its oxidation to the radical cation  $4\cdot^+$  should be a facile reaction. Indeed we have succeeded in preparing both the radical ions  $4\cdot^+$  and  $4\cdot^-$  which are isoelectronic with the phenalenyl radical ( $5\cdot$ ) and the corresponding radical dianion ( $5\cdot$ )<sup>2-</sup>, respectively. In the present paper we describe the esr spectra of  $4\cdot^+$  and  $4\cdot^-$ , in addition to those of the radical ions  $4a\cdot^+$ ,  $4a\cdot^-$ ,  $4b\cdot^+$ , and  $4b\cdot^-$  produced from the 1,3-dicyano derivative (**4a**) and the 1,3-di-*tert*-butyl ester (**4b**). ESR data are also reported for the radical anion  $4c\cdot^-$  of the *tert*-butyl monoester (**4c**) which was obtained as an intermediate in the decarboxylation reaction  $4b \rightarrow 4$ .



- 4**, R = R' = H  
**a**, R = R' = CN  
**b**, R = R' = COOC(CH<sub>3</sub>)<sub>3</sub>  
**c**, R = COOC(CH<sub>3</sub>)<sub>3</sub>; R' = H

## Experimental Section

**Source of Compounds.** The synthesis of the 1,3-di-*tert*-butyl ester (**4b**) and the parent cycl[3.3.3]azine (**4**) has been described elsewhere.<sup>7</sup> The 1,3-dicyano derivative (**4a**) was prepared from quinolizin-4-ylideneacetonitrile by reaction with cyanoacetylene in boiling nitrobenzene.<sup>12</sup>

Since the parent compound **4** is sensitive to oxygen, it was preferably produced in small quantities from the diester **4b** immediately before its further conversion to the radical ion  $4\cdot^+$  or  $4\cdot^-$ . The following procedure proved to be adequate for the thermal decarboxylation of **4b**. An evacuated capillary containing  $\sim 10$  mg of **4b** was heated to  $+270^\circ$  for 10 min. The capillary was then opened in a nitrogen atmosphere and transferred into the side arm of an esr sample tube. High-vacuum sublimation of the decarboxylation product at  $+100^\circ$  yielded 1–2 mg of crystallized cyclazine **4** for the subsequent oxidation or reduction to  $4\cdot^+$  or  $4\cdot^-$ , respectively.

When the thermal decarboxylation of the diester **4b** was incomplete, the sublimed crystals consisted mainly of the intermediate monoester **4c** with varying amounts of **4** and **4b**.

**Preparation of the Radical Ions.** The neutral compounds **4**, **4a**, and **4b** were oxidized to their radical cations  $4\cdot^+$ ,  $4a\cdot^+$ , and  $4b\cdot^+$  by reaction with the Ag<sup>+</sup> ion (perchlorate or tetrafluoroborate) in thoroughly dried and degassed acetonitrile (ACN) or 1,2-dimethoxyethane (DME). The radical cations produced in this way could be stored for days at room temperature without an appreciable decrease in concentration.

The reduction of the neutral compounds **4**, **4a**, and **4b** to their radical anions  $4\cdot^-$ ,  $4a\cdot^-$ , and  $4b\cdot^-$  was performed by reaction with an alkali metal (Na or K) in DME or by electrolysis in *N,N'*-dimethylformamide (DMF) with tetraethylammonium perchlorate as supporting salt. For the parent cyclazine **4**, reaction with alkali metal was preferred over electrolytical reduction, since (1) it is a more convenient means of handling compounds sensitive to oxygen and protic impurities, and (2) the relatively low electron affinity of **4**<sup>13</sup> makes a strong reducing agent desirable. On the other hand, electrolytical reduction led to esr spectra of better quality for the disubstituted derivatives **4a** and **4b**. Although the radical anions were less stable than the corresponding cations, they exhibited sufficient stability for esr studies.

Conversion of the monoester **4c** to its radical ions  $4c\cdot^+$  or  $4c\cdot^-$  presented additional problems. As stated above, the compound **4c** was obtained upon an incomplete decarboxylation of the diester

(12) D. Leaver and T. T. Gough, unpublished results.

(13) Cycl[3.3.3]azine (**4**) is estimated to have a higher electron affinity than diphenyl, but a lower one than naphthalene.

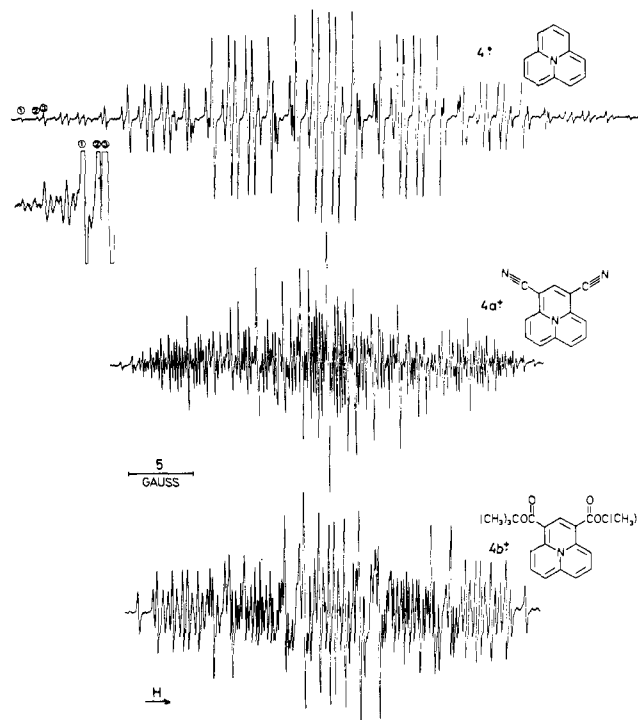


Figure 1. ESR spectra of the radical cations  $4\cdot^+$ ,  $4a\cdot^+$ , and  $4b\cdot^+$ : solvent, ACN ( $4\cdot^+$  and  $4a\cdot^+$ ) or DME ( $4b\cdot^+$ ); counterion, ClO<sub>4</sub><sup>-</sup> ( $4\cdot^+$  and  $4b\cdot^+$ ) or BF<sub>4</sub><sup>-</sup> ( $4a\cdot^+$ ); temperature,  $+30^\circ$  ( $4\cdot^+$ ),  $-60^\circ$  ( $4a\cdot^+$ ), or  $-30^\circ$  ( $4b\cdot^+$ ). Below the spectrum of  $4\cdot^+$ , the low-field part, taken under higher amplification, is reproduced. Numbers ①, ②, and ③ mark the outermost hyperfine lines due to the radical cations  $4\cdot^+$  not containing <sup>13</sup>C isotopes.

**4b** and contained varying amounts of **4b** and the unsubstituted cyclazine **4**. Oxidation of this material with the Ag<sup>+</sup> ion yielded mixtures of the three radical cations  $4\cdot^+$ ,  $4b\cdot^+$ , and  $4c\cdot^+$ , the esr spectra of which could not be analyzed for the data of  $4c\cdot^+$ . In contrast, it was possible to carry out a stepwise reduction with an alkali metal, producing the radical anions in the sequence  $4b\cdot^-$ ,  $4c\cdot^-$ ,  $4\cdot^-$ , which reflects the decreasing electron affinity of the neutral compounds. In particular, the esr spectrum of  $4c\cdot^-$ , unaffected by the signals of either  $4b\cdot^-$  or  $4\cdot^-$ , was observed after the decay of  $4b\cdot^-$  and upon a renewed contact of the solution with the alkali metal. This spectrum could be reliably analyzed and interpreted (see below).

## Results

Figure 1 shows the esr spectra of the radical cations  $4\cdot^+$ ,  $4a\cdot^+$ , and  $4b\cdot^+$ . The spectrum of the unsubstituted cation  $4\cdot^+$  exhibits seven groups of lines indicating a major splitting by six equivalent protons. This spectrum is reminiscent of that observed for the isoelectronic phenalenyl radical ( $5\cdot$ ).<sup>14–16</sup> Substitution in the 1,3 positions of  $4\cdot^+$  to yield  $4a\cdot^+$  or  $4b\cdot^+$  strongly reduces the total extension of the spectrum, because the main splittings now stem from only four protons.

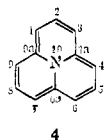
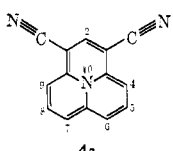
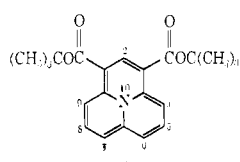
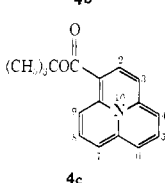
Figure 2 presents the esr spectra of the radical anions  $4\cdot^-$ ,  $4a\cdot^-$ , and  $4b\cdot^-$ ; that of  $4c\cdot^-$  is reproduced in Figure 3a. The extreme simplicity of the hyperfine pattern in the spectrum of the unsubstituted anion  $4\cdot^-$  (12 lines) is due to the fact that only the splittings by three equivalent ring protons and one <sup>14</sup>N nucleus are resolved. The total extension of the spectrum is

(14) P. B. Sogo, M. Nagazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957); J. E. Bennett, *Nature (London)*, **188**, 485 (1960); *Proc. Chem. Soc., London*, 144 (1961).

(15) F. Gerson, *Helv. Chim. Acta*, **49**, 1463 (1966).

(16) H. Falle and G. R. Luckhurst, *Mol. Phys.*, **11**, 299 (1966); S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **44**, 2884 (1966).

Table I. Hyperfine Coupling Constants for the Radical Ions of 4, 4a, 4b, and 4c

Radical ion of	No. of nuclei	Coupling constants, G		Assignment to positions	
		Cation	Anion		
 4	6 $^1\text{H}$	$6.45 \pm 0.03$	$0.05 \pm 0.01^{a,b}$	1,3,4,6,7,9	
	3 $^1\text{H}$	$1.78 \pm 0.01$	$4.84 \pm 0.03$	2,5,8	
	1 $^{14}\text{N}$	$1.29 \pm 0.01$	$6.54 \pm 0.03$	10	
	6 $^{13}\text{C}$	$9.69 \pm 0.08$	$4.47 \pm 0.05$	1,3,4,6,7,9	
	3 $^{13}\text{C}$	$8.71 \pm 0.08^c$	$6.56 \pm 0.05$	2,5,8	
	3 $^{13}\text{C}$	$7.73 \pm 0.08^c$	$1.62 \pm 0.05$	3a, 6a, 9a	
	 4a	2 $^1\text{H}$	$5.43 \pm 0.04$	$0.50 \pm 0.03$	4,9 or 6,7
2 $^1\text{H}$		$5.34 \pm 0.04$	$0.43 \pm 0.03$	6,7 or 4,9	
2 $^1\text{H}$		$1.40 \pm 0.02$	$5.08 \pm 0.05$	5,8	
1 $^1\text{H}$		$2.00 \pm 0.03$	$5.49 \pm 0.05$	2	
1 $^{14}\text{N}$		$1.01 \pm 0.02$	$5.96 \pm 0.05$	10	
2 $^{14}\text{N}$		$0.82 \pm 0.02$	$0.09 \pm 0.03^{a,b}$	Cyano	
 4b		2 $^1\text{H}$	$5.71 \pm 0.04$	$0.70 \pm 0.01$	4,9 or 6,7
	2 $^1\text{H}$	$5.54 \pm 0.04$	$0.26 \pm 0.01$	6,7 or 4,9	
	2 $^1\text{H}$	$1.51 \pm 0.01$	$5.28 \pm 0.04$	5,8	
	1 $^1\text{H}$	$1.95 \pm 0.01$	$4.71 \pm 0.04$	2	
	1 $^{14}\text{N}$	$1.19 \pm 0.01$	$6.17 \pm 0.04$	10	
	9 $^1\text{H}$	$<0.04^a$	$<0.02^a$	<i>tert</i> -Butyl	
	 4c	3 $^1\text{H}$		$0.62 \pm 0.03$	3,4,6,7,9
		2 $^1\text{H}$		$0.30 \pm 0.03$	
		1 $^1\text{H}$		$6.46 \pm 0.05$	5 or 8
1 $^1\text{H}$			$4.59 \pm 0.05$	2	
1 $^1\text{H}$			$3.95 \pm 0.03$	8 or 5	
1 $^{14}\text{N}$			$6.14 \pm 0.05$	10	
9 $^1\text{H}$		$<0.02^a$	<i>tert</i> -Butyl		

<sup>a</sup> Splitting unresolved. <sup>b</sup> Value obtained by computer simulation of the spectrum. <sup>c</sup> A reverse assignment of these two coupling constants cannot be excluded (see Discussion).

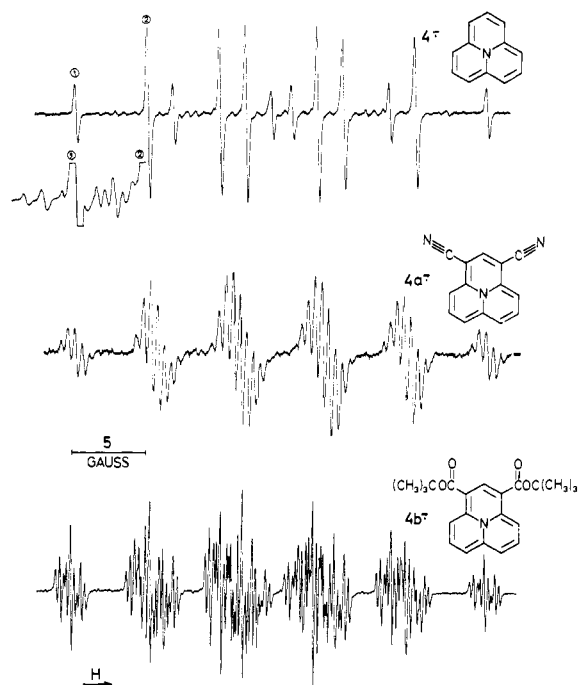


Figure 2. ESR spectra of the radical anions  $4\cdot^-$ ,  $4a\cdot^-$ , and  $4b\cdot^-$ : solvent, DME ( $4\cdot^-$ ) or DMF ( $4a\cdot^-$  and  $4b\cdot^-$ ); counterion,  $\text{K}^+$  ( $4\cdot^-$ ) or  $(\text{C}_2\text{H}_5)_4\text{N}^+$  ( $4a\cdot^-$  and  $4b\cdot^-$ ); temperature,  $-20^\circ$ . Below the spectrum of  $4\cdot^-$ , the low-field part, taken under higher amplification, is reproduced. Numbers ① and ② mark the outermost lines due to the radical anions  $4\cdot^-$  not containing  $^{13}\text{C}$  isotopes.

not greatly altered on passing to the substituted radical anions  $4a\cdot^-$ ,  $4b\cdot^-$ , and  $4c\cdot^-$ , for which the major hyperfine splittings also arise from three protons and one  $^{14}\text{N}$  nucleus, giving the six observed groups of lines.

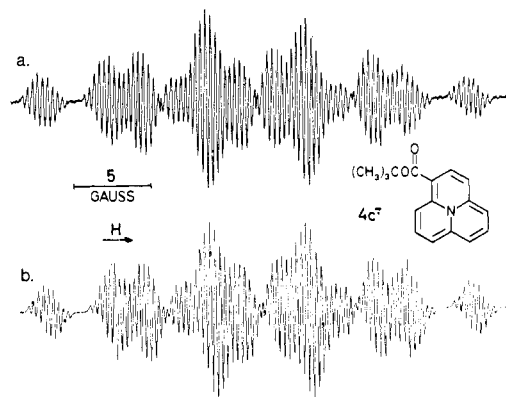


Figure 3. (a) ESR spectrum of the radical anion  $4c\cdot^-$ : solvent, DME; counterion,  $\text{K}^+$ ; temperature,  $-20^\circ$ . (b) Computer-simulated spectrum: coupling constants see Table I; line-form Lorentzian; line width 0.14 G. (The computed curve does not account for a slight selective line broadening caused by  $^{14}\text{N}$  hyperfine anisotropy.)

Changes of temperature in the range of  $-60$  to  $+30^\circ$  slightly affect the resolution of the spectra, but do not markedly alter the hyperfine splittings for any of the radical cations and anions. Table I lists the proton and  $^{14}\text{N}$  coupling constants resulting from an extensive, computer-assisted analysis of the spectra. To save space and to preserve the lucidity of Figures 1 and 2 we have not reproduced the calculated curves. The degree of agreement between experiment and simulation is demonstrated by Figure 3b which shows a computed spectrum of  $4c\cdot^-$  below its observed counterpart (Figure 3a). The result is remarkable for a radical ion containing one  $^{14}\text{N}$  nucleus, eight nonequivalent ring protons, and nine *tert*-butyl

protons. The success of the analysis must in this case be largely attributed to the fact that (1) some of the smaller ring proton coupling constants are equal within the limits of experimental accuracy, and (2) the *tert*-butyl proton splittings are too small to be resolved.

The assignment of the  $^{14}\text{N}$  and proton coupling constants is straightforward for the unsubstituted radical ions  $4\cdot^-$  and  $4\cdot^+$  which contain a single  $^{14}\text{N}$  nucleus and sets of six and three equivalent protons in positions 1,3,4,6,7,9 and 2,5,8, respectively. In the case of the disubstituted radical ions  $4a\cdot^+$ ,  $4b\cdot^+$ ,  $4a\cdot^-$ , and  $4b\cdot^-$ , coupling constants can also be directly assigned for the  $^{14}\text{N}$  nucleus of the central nitrogen atom and the single proton in position 2. The remaining ring protons in positions 3–9 of these radical ions are pairwise equivalent, and the assignment made in Table I for their coupling constants is based on the reasonable assumption that the substitution does not drastically alter the  $\pi$ -spin distribution in  $4\cdot^+$  and  $4\cdot^-$ . Such an assumption which leads to a consistent interpretation of the substituent effects (see Discussion) implies the following statements.

(1) For the radical cations  $4a\cdot^+$  and  $4b\cdot^+$ , the coupling constants of the protons in positions 4,9 and 6,7 must be considerably larger ( $>5$  G) than those of the 5,8 protons ( $<2$  G).

(2) The opposite should be true for the radical anions  $4a\cdot^-$  and  $4b\cdot^-$ . In this case, the coupling constants of the proton in positions 4,9 and 6,7 are expected to be very small ( $<1$  G), whereas those of the 5,8 protons ought to be of relatively larger magnitude ( $>4$  G).

The last argument also justifies the partial assignment of the ring proton coupling constants for the monosubstituted radical anion  $4c\cdot^-$ . Moreover, use of the additivity model<sup>17</sup> for the effect of the  $\text{COOC}(\text{CH}_3)_3$  substituent in the series  $4\cdot^-$ ,  $4c\cdot^-$ ,  $4b\cdot^-$  suggests that, of the three large coupling constants found for the nonequivalent 2,5,8 protons of  $4c\cdot^-$ , the medium-sized one may be assigned to position 2.

The hyperfine splittings arising from the magnetic nuclei in the substituents are generally too small to be resolved ( $<0.1$  G). The only exception is the splitting ( $\sim 0.8$  G) observed for the two equivalent  $^{14}\text{N}$  nuclei in the cyano groups of the radical cation  $4a\cdot^+$ .

Below the spectra of  $4\cdot^-$  (Figure 1) and  $4\cdot^+$  (Figure 2), the pertinent low-field sections, taken under higher amplification, are reproduced. They display satellite lines due to the  $^{13}\text{C}$  nuclei in natural abundance. The assignment of the  $^{13}\text{C}$  coupling constants (listed in Table I) to sets of equivalent carbon sites (one set of six and two of three) is based partly on the relative intensities of the satellite lines and partly on correlation with the values estimated by means of current formulas<sup>18</sup> (see Discussion). Although analogous satellite spectra were also observed for the substituted radical ions, their complexity, caused by the large numbers of nonequivalent carbon sites, impeded an unambiguous analysis.

The radical cations  $4\cdot^+$ ,  $4a\cdot^+$ , and  $4b\cdot^+$  have  $g$

(17) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959); B. L. Barton and G. K. Fraenkel, *ibid.*, **41**, 1455 (1964).

(18) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

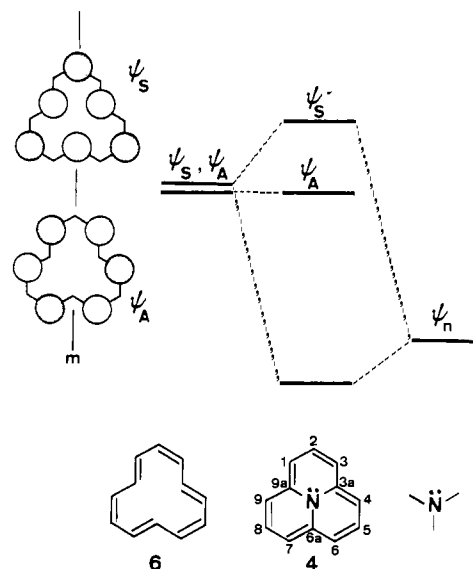


Figure 4. Correlation diagram for the degenerate nonbonding orbitals ( $\psi_S$  and  $\psi_A$ ) of the [12]annulene (6) and the two frontier orbitals (HOMO  $\psi_A$  and LUMO  $\psi_S'$ ) of cycl[3.3.3]azine (4). In the schematical representation of  $\psi_S$  and  $\psi_A$ , shadowed and empty circles refer to the alternating signs of the LCAO coefficients which have the same absolute value of  $1/\sqrt{6}$ . Only one of the three mirror planes  $m$  is indicated by its trace.

values of 2.0027, 2.0028, and 2.0031, respectively. The  $g$  values of the radical anions  $4\cdot^-$ ,  $4a\cdot^-$ ,  $4b\cdot^-$ , and  $4c\cdot^-$  are all 2.0030 within  $\pm 0.0001$ .

## Discussion

**$\pi$ -Spin Populations.** The doubly degenerate nonbonding orbitals of [12]annulene (6) are a good starting point for the discussion of the  $\pi$ -spin distribution in the radical ions of cycl[3.3.3]azine (4). These perimeter orbitals, depicted schematically in Figure 4, have been classified as symmetric ( $\psi_S$ ) and antisymmetric ( $\psi_A$ ) with regard to mirror planes ( $m$ ) passing through two opposite  $\pi$  centers and perpendicular to the molecular plane. The symmetric orbital  $\psi_S$  exhibits nonvanishing LCAO coefficients ( $\pm 1/\sqrt{6}$ ) solely at the six centers situated in one of the three planes  $m$ , whereas for its antisymmetric counterpart  $\psi_A$  such coefficients ( $\pm 1/\sqrt{6}$ ) are found only at the six remaining centers. One notes that the centers with the nonzero coefficients of  $\psi_S$  and  $\psi_A$  correspond in cycl[3.3.3]azine to positions 2,3a,5,6a,8,9a and 1,3,4,6,7,9, respectively (Figure 4).

Introduction of the central nitrogen atom ( $\ddot{\text{N}}$ ) into [12]annulene (6) to yield cycl[3.3.3]azine (4) removes the degeneracy of  $\psi_S$  and  $\psi_A$ . Since this atom lies in the nodal planes  $m$  of the antisymmetric orbital  $\psi_A$ , the latter is, to a first approximation, not affected by the nitrogen lone pair function  $\psi_n$ . In contrast, its symmetric counterpart  $\psi_S$  strongly mixes with  $\psi_n$ , and the resulting orbital  $\psi_S'$  is pushed to higher energies (Figure 4). The following predictions can thus be made for the two frontier orbitals of 4: the highest occupied MO (HOMO) should be well represented by the nonbonding perimeter orbital  $\psi_A$ , whereas the lowest unoccupied MO (LUMO) is expected to be an antibonding orbital ( $\psi_S'$ ) which correlates with the nonbonding perimeter orbital  $\psi_S$ . These predictions are nicely confirmed by the esr data for the radical ions  $4\cdot^+$  and

**Table II.** "Experimental" and "Theoretical"  $\pi$ -Spin Populations ( $\rho_\mu$ ) in the Cycl[3.3.3]azine Radical Ions ( $4\cdot^+$  and  $4\cdot^-$ ) and the Phenalenyl Radical ( $5\cdot$ )

Position $\mu$	Cation $4\cdot^+$			Anion $4\cdot^-$			Phenalenyl $5\cdot$		
	$a_{H\mu}$ , G	$\rho_\mu^{\text{exptl}}$	$\rho_\mu^{\text{theor}}$	$a_{H\mu}$ , G	$\rho_\mu^{\text{exptl}}$	$\rho_\mu^{\text{theor}}$	$a_{H\mu}$ , G	$\rho_\mu^{\text{exptl}}$	$\rho_\mu^{\text{theor}}$
1,3,4,6,7,9	(-) $6.45^a$	(+) $0.215^{a,b}$	+ $0.218^c$	(+) $0.05^a$	(-) $0.002^{a,b}$	- $0.019^c$	- $6.29^d$	+ $0.217^b$	+ $0.218^c$
2,5,8	(+) $1.78^a$	(-) $0.059^{a,b}$	- $0.059^c$	(-) $4.84^a$	(+) $0.193^{a,b}$	+ $0.192^c$	+ $1.81^d$	- $0.062^b$	- $0.060^c$
3a,6a,9a			- $0.045^c$			+ $0.112^c$			- $0.045^c$
10			+ $0.003^c$			+ $0.204^c$			+ $0.005^c$

<sup>a</sup> Sign required by theory. <sup>b</sup> Obtained from  $a_{H\mu}$  with the aid of eq 1; see text. <sup>c</sup> Calculated by means of McLachlan procedure; see text. <sup>d</sup> Taken from ref 15 with sign determined in ref 16 by studies on liquid crystal solutions.

**Table III.** Calculated and Observed  $^{13}\text{C}$  Coupling Constants ( $a_{C\mu}^{\text{calcd}}$  and  $a_{C\mu}^{\text{obsd}}$  in G) for the Cycl[3.3.3]azine Radical Ions ( $4\cdot^+$  and  $4\cdot^-$ ) and the Phenalenyl Radical ( $5\cdot$ )

Position $\mu$	Cation $4\cdot^+$		Anion $4\cdot^-$		Phenalenyl $5\cdot$	
	$a_{C\mu}^{\text{calcd}}$	$a_{C\mu}^{\text{obsd}}$	$a_{C\mu}^{\text{calcd}}$	$a_{C\mu}^{\text{obsd}}$	$a_{C\mu}^{\text{calcd}}$	$a_{C\mu}^{\text{obsd}}$
1,3,4,6,7,9	+ $9.22^a$	(+) $9.69^b$	- $4.92^a$	(-) $4.47^b$	+ $9.25^a$	+ $9.66^c$
2,5,8	- $8.17^a$	(-) $8.71^b$	+ $7.38^a$	(+) $6.56^b$	- $8.23^a$	- $7.84^c$
3a,6a,9a	- $7.49^a$	(-) $7.73^b$	+ $1.11^a$	(+) $1.62^b$	- $7.52^a$	- $7.84^c$

<sup>a</sup> Obtained from  $\rho_\mu^{\text{theor}}$  (Table II) with the aid of eq 2 and the parameters proposed in ref 18; see text. <sup>b</sup> Sign required by theory. <sup>c</sup> Taken from ref 15 with sign determined in ref 16 by studies on liquid crystal solutions.

$4\cdot^-$  (Table I). The electron distribution in the singly occupied MO  $\psi_A$  of the cation  $4\cdot^+$  is reflected by the finding that the six equivalent protons in positions 1,3,4,6,7,9 have a *much larger* coupling constant (6.45 G) than the three equivalent 2,5,8 protons (1.78 G) and the  $^{14}\text{N}$  nucleus (1.29 G). On the other hand, the reverse order observed for the corresponding values of the anion  $4\cdot^-$  is in accordance with the single occupancy of the MO  $\psi_{S'}$ , a  $\psi_S$ -like orbital with a strong admixture of  $\psi_n$ . In this case, the coupling constants of the three equivalent protons in positions 2,5,8 (4.84 G) and the  $^{14}\text{N}$  nucleus (6.54 G) are *large*, whereas that of the six equivalent 1,3,4,6,7,9 protons (0.05 G) is *very small*.

The qualitative relationship between the perimeter MO model and the esr data for  $4\cdot^-$  and  $4\cdot^+$  is substantiated by conventional calculations of the  $\pi$ -spin distribution. Use of the standard HMO parameter<sup>19</sup>  $\alpha_{\dot{N}} = \alpha + 1.5\beta$  for the Coulomb integral of the central nitrogen atom yields the energies  $E(\psi_A) = \alpha$  and  $E(\psi_{S'}) = \alpha - 0.63\beta$  for the nonbonding HOMO and the antibonding LUMO of  $4$ , respectively. Table II lists the carbon  $\pi$ -spin populations,  $\rho_\mu^{\text{theor}}$ , calculated by the McLachlan<sup>20</sup> procedure (parameter  $\lambda = 1.0$ ) for the single occupancy of  $\psi_A$  in  $4\cdot^+$  and  $\psi_{S'}$  in  $4\cdot^-$ . There is an excellent agreement between the "theoretical" values  $\rho_\mu^{\text{theor}}$  and their "experimental" counterparts  $\rho_\mu^{\text{exptl}}$  which are given in Table II for the proton-bearing centers  $\mu$ . The latter were obtained from the observed proton coupling constants  $a_{H\mu}$  with the aid of the McConnell<sup>21</sup> equation

$$a_{H\mu} = Q_{CH^H} \rho_\mu \quad (1)$$

where the values of  $-30$  and  $-25$  G have been adopted for  $Q_{CH^H}$  in the case of  $4\cdot^+$  and  $4\cdot^-$ , respectively.<sup>22</sup>

(19) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 135; (b) *ibid.*, pp 454-457; (c) *ibid.*, pp 104-106.

(20) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(21) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(22) This differentiation should account for the well-known fact that comparable  $\pi$ -spin populations  $\rho_\mu$  give rise to larger coupling constants  $a_{H\mu}$  for the radical cations than for the anions. See, e.g., F. Gerson, "High Resolution E. S. R. Spectroscopy," Wiley, New York, N. Y., 1967, Chapter 2.1; or J. R. Bolton in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, Chapter I.

Table II also contains the  $\pi$ -spin populations  $\rho_\mu^{\text{theor}}$  and  $\rho_\mu^{\text{exptl}}$  for the phenalenyl radical ( $5\cdot$ ) which, as mentioned above, is isoelectronic with  $4\cdot^+$ . The almost identical values of  $\rho_\mu^{\text{theor}}$  for the two radicals are in perfect accord with our MO model which demands that in both species the singly occupied orbital should, to a first approximation, be represented by the unperturbed perimeter orbital  $\psi_A$ . Similarly, the  $\pi$ -spin populations  $\rho_\mu^{\text{exptl}}$  are found to be nearly identical for  $4\cdot^+$  and  $5\cdot$  if a value  $Q_{CH^H} = -29$  G is taken for  $5\cdot$  in eq 1.

**$^{13}\text{C}$  and  $^{14}\text{N}$  Coupling Constants.** The good agreement between theory and experiment suggests the use of the  $\pi$ -spin populations  $\rho_\mu^{\text{theor}}$  for the estimation of the  $^{13}\text{C}$  coupling constants in  $4\cdot^+$  and  $4\cdot^-$ . The estimated values  $a_{C\mu}^{\text{calcd}}$  given in Table III were calculated according to eq 2 in which  $\mu$  refers to the pertinent

$$a_{C\mu} = (S^C + \sum_\nu Q_{CX\nu^C}) \rho_\mu + \sum_\nu Q_{X\nu^C} \rho_\nu \quad (2)$$

carbon site and  $\nu$  to a neighboring atom X. The originally proposed<sup>18</sup> parameters  $S^C = -12.7$ ,  $Q_{CH^C} = +19.5$ ,  $Q_{CC\nu^C} = +14.4$ , and  $Q_{C\nu^C} = -13.9$  G were used, the two latter also serving as substitutes for the unavailable values of  $Q_{CN\nu^C}$  and  $Q_{N\nu^C}$ , respectively. The  $a_{C\mu}^{\text{calcd}}$  values resulting in this way agree fairly well with their experimental counterparts  $a_{C\mu}^{\text{obsd}}$  which are also listed in Table III.

The assignment made in Table III and justified by the correlation between  $a_{C\mu}^{\text{calcd}}$  and  $a_{C\mu}^{\text{obsd}}$  can, however, be challenged for the coupling constants 8.71 and 7.73 G ( $4\cdot^+$ :  $\mu = 2,5,8$  and 3a,6a,9a) if the experimental data for the cation  $4\cdot^+$  are compared with those of the isoelectronic radical  $5\cdot$ . Since the  $\pi$ -spin populations  $\rho_\mu^{\text{theor}}$  are almost identical in  $4\cdot^+$  and  $5\cdot$ , and since exactly the same parameters were used for both radicals in eq 2 (see above), the values  $a_{C\mu}^{\text{calcd}}$  of  $4\cdot^+$  and  $5\cdot$  are nearly equal. As evident from Table III, the expectation that this would also hold for  $a_{C\mu}^{\text{obsd}}$  is not completely borne out by experiment, a significant difference being found for one coupling constant due to  $^{13}\text{C}$  nuclei in three equivalent carbon sites. One may argue that such a difference should occur rather for  $\mu = 3a,6a,9a$  than for 2,5,8, because the carbon atoms in the former positions have different neighbors  $\nu$  in  $4\cdot^+$

**Table IV.** Observed and Estimated  $^{14}\text{N}$  Coupling Constants ( $a_{\text{N}\mu}$  in G) for the Central Nitrogen Atoms in the Radical Ions of Cycl[3.2.2]azine (1), Cycl[3.3.3]azine (4), and Cyclopenta[*h*]cycyl[4.2.2]azine (7)

Radical ion	$\rho_{\mu}^{\text{theor}}$	$\sum_{\nu}\rho_{\nu}^{\text{theor}}$	$a_{\text{N}\mu}^{\text{calcd}}$	$a_{\text{N}\mu}^{\text{obsd}}$
1 $\cdot^{-}$	-0.010 <sup>a</sup>	-0.039 + 2(+0.051) <sup>a</sup>	-0.8 ± 0.2 <sup>b</sup>	(-)0.60 <sup>c,d</sup>
4 $\cdot^{+}$	+0.003 <sup>a</sup>	3(-0.045) <sup>a</sup>	+1.0 ± 0.3 <sup>b</sup>	(+)1.29 <sup>d</sup>
4 $\cdot^{-}$	+0.204 <sup>a</sup>	3(+0.112) <sup>a</sup>	+5.8 ± 1.5 <sup>b</sup>	(+)6.54 <sup>d</sup>
7 $\cdot^{-}$	+0.046 <sup>a</sup>	+0.082 + 2(-0.043) <sup>a</sup>	+1.8 ± 0.2 <sup>b</sup>	(+)1.55 <sup>d,e</sup>

<sup>a</sup> Calculated by means of McLachlan procedure; see text. <sup>b</sup> Obtained from  $\rho_{\mu}^{\text{theor}}$  with the aid of eq 3 and the parameters given in the text. <sup>c</sup> Taken from ref 6. <sup>d</sup> Sign required by theory. <sup>e</sup> Taken from ref 10.

(X = N) and 5 $\cdot$  (X = C). This argument thus favors an assignment opposite to that in Table III, as it requires for 4 $\cdot^{+}$  that the differing value of 8.71 G should be assigned to  $\mu = 3a, 6a, 9a$ , leaving 7.73 G to  $\mu = 2, 5, 8$ .

A formula analogous to eq 2 could be used for the estimation of the  $^{14}\text{N}$  coupling constants if the parameters relating the values  $a_{\text{N}\mu}$  to the  $\pi$ -spin populations  $\rho_{\mu}$  and  $\rho_{\nu}$  were known. Unfortunately, this is not the case for a nitrogen  $\mu$  bound to three carbon centers  $\nu$ , as in 4 $\cdot^{+}$  and 4 $\cdot^{-}$ . A converse procedure was therefore adopted in which the pertinent parameters were determined empirically from the available values  $a_{\text{N}\mu}$  of four unsubstituted cyclazine radical ions. The simplified eq 3 had to be applied with  $Q_{\text{N}^{\text{N}}} = S^{\text{N}} + 3Q_{\text{CN}^{\text{C}}}$ ,

$$a_{\text{N}\mu} = Q_{\text{N}^{\text{N}}}\rho_{\mu} + Q_{\text{CN}^{\text{C}}}\sum_{\nu}\rho_{\nu} \quad (3)$$

since the individual parameters in such a sum cannot be evaluated separately.<sup>23</sup> The four radical ions, which provide the  $^{14}\text{N}$  coupling constants for this procedure, are the anions 1 $\cdot^{-}$  and 7 $\cdot^{-}$  of cycl[3.2.2]azine<sup>6</sup> and cyclopenta[*h*]cycyl[4.2.2]azine,<sup>10</sup> respectively, in addition to the two ions 4 $\cdot^{+}$  and 4 $\cdot^{-}$  of cycl[3.3.3]azine. Table IV lists these coupling constants ( $a_{\text{N}\mu}^{\text{obsd}}$ ), along with the  $\pi$ -spin populations  $\rho_{\mu}^{\text{theor}}$  and  $\sum_{\nu}\rho_{\nu}^{\text{theor}}$  required for eq 3 and calculated by the same McLachlan procedure ( $\alpha_{\text{N}}^{\text{N}} = \alpha + 1.5\beta$ ;  $\lambda = 1.0$ ). Insertion into eq 3 yields  $+39 \pm 4$  and  $-6.5 \pm 2$  G as reasonable estimates for the parameters  $Q_{\text{N}^{\text{N}}}$  and  $Q_{\text{CN}^{\text{C}}}$ , respectively. Such parameters reproduce the coupling constants  $a_{\text{N}\mu}^{\text{obsd}}$  within the error limits, as demonstrated by the values  $a_{\text{N}\mu}^{\text{calcd}}$  which are also given in Table IV. Moreover, they compare favorably in magnitude and sign with analogous empirical parameters reported in the literature for  $\text{sp}^2$ -hybridized carbon<sup>18, 23</sup> and nitrogen atoms.<sup>24</sup> This result suggests that the position of the central nitrogen atom in the cyclazine radical ions does not greatly deviate from the plane of the cyclic  $\pi$  system, since an appreciable change in the hybridization would lead to quite different values of  $Q_{\text{N}^{\text{N}}}$  and  $Q_{\text{CN}^{\text{C}}}$ .<sup>25</sup>

**"Aromaticity" of Cycl[3.3.3]azine Radical Ions.** By means of SCF-MO calculations, Dewar and Trinajstić<sup>9</sup> have predicted that the radical cation 4 $\cdot^{+}$  of cycl[3.3.3]azine should be "aromatic" with no essential double bond localization (symmetry  $D_{3h}$ ), in contrast to the neutral compound 4 which exhibits alternating essential single and double bonds (symmetry  $C_{3h}$ ); no consideration was given to the radical anion 4 $\cdot^{-}$ . We have treated both ions 4 $\cdot^{+}$  and 4 $\cdot^{-}$  as aromatic  $\pi$  systems displaying an unimpaird cyclic conjugation

over the 12-membered ring. Such a treatment cannot, however, be justified solely by the fact that the experimental coupling constants reflect the symmetry  $D_{3h}$ , since the same result would also be obtained if the interconversion between two equivalent structures of symmetry  $C_{3h}$  were rapid on the esr scale.<sup>26</sup> It would therefore be desirable to calculate the optimal geometry for 4 $\cdot^{-}$ , by a method analogous to that used for 4 $\cdot^{+}$  and 4.<sup>9</sup> Nevertheless, two arguments supporting the aromaticity of 4 $\cdot^{-}$  can be put forward without any further calculations.

(1) One may resort to the Hückel rule and take the total  $\pi$ -electron charge  $\sum_{\mu}q_{\mu}$  on the 12-membered perimeter as a criterion of aromaticity. Since the HMO charges  $q_{\mu}$  are known to be highly unreliable,<sup>19b</sup> it is preferable to start with the SCF value for 4<sup>9</sup> and use the HMO model only for the contributions due to the HOMO and LUMO. This procedure yields  $\sum_{\mu}q_{\mu} = 11.17, 12.17,$  and  $12.99$  for 4 $\cdot^{+}, 4,$  and 4 $\cdot^{-}$ , respectively. Whereas the value for the neutral compound 4 is close to 12, as in the antiaromatic [12]annulene (6),<sup>27</sup> those for the radical ions clearly approach the Hückel ( $2 + 4n$ ) numbers, 10(4 $\cdot^{+}$ ) and 14(4 $\cdot^{-}$ ). In the latter case, analogy to cyclooctatetraene can be invoked where the radical anion having nine  $\pi$  electrons is regarded as planar and aromatic, in contrast to the olefinic neutral compound with eight  $\pi$  electrons.<sup>28</sup>

(2) The  $\pi$ -spin populations  $\rho_{\mu}^{\text{theor}}$  calculated for two rapidly interconverting structures with bond alternation differ distinctly from those given in Table II. In these calculations carried out by means of the McLachlan procedure,<sup>20</sup> double and single bonds were simulated with the aid of parameters  $\beta_{\text{C}=\text{C}} = 1.1-1.2\beta$  and  $\beta_{\text{C}-\text{C}} = 0.8 - 0.9\beta$ ,<sup>19c</sup> and the interconversion was allowed for by averaging the values  $\rho_{\mu}^{\text{theor}}$  for the two structures. Significant results are decreased values  $\rho_{\mu}^{\text{theor}}$  at the carbon centers  $\mu$  of high  $\pi$ -spin population (4 $\cdot^{+}$ :  $\mu = 1, 3, 4, 6, 7, 9$ ; 4 $\cdot^{-}$ :  $\mu = 2, 5, 8$ ) relative to the numbers found for the aromatic radical ions (Table II). Such a decrease leads to less agreement with experiment, since it implies an unreasonable increase in the parameter  $Q_{\text{CH}^{\text{H}}}$  of eq 1 in order to match the observed proton coupling constants  $a_{\text{H}\mu}$ .

**Effect of Substitution.** Since several additional

(26) Lowering of the symmetry from  $C_{3h}$  to  $C_s$ , as a consequence of double bond localization, was observed by esr spectroscopy for the radical anion of *anti*-bis-1,6:8,13-methano[14]annulene: F. Gerson, K. Müllen, and E. Vogel, *J. Amer. Chem. Soc.*, **94**, 2924 (1972). In this case, the interconversion between two structures of symmetry  $C_s$  must be slow on the esr scale.

(27) J. F. Oth, H. Röttle, and G. Schröder, *Tetrahedron Lett.*, **37**, 3251 (1970); J. F. M. Oth and G. Schröder, *J. Chem. Soc. B*, 904 (1971).

(28) See, e.g., F. Gerson and J. H. Hammons in "Nonbenzenoid Aromatics," Vol. II, S. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, pp 96-99.

(23) E. T. Strom, G. R. Underwood, and D. Jurkowitz, *Mol. Phys.*, **24**, 901 (1972).

(24) F. Gerson, *Mol. Phys.*, **24**, 445 (1972), and references therein.

(25) See, e.g., F. Gerson, E. Haselbach, and G. Plattner, *Chem. Phys. Lett.*, **12**, 316 (1971).

**Table V.**  $^{14}\text{N}$  and Averaged Proton Coupling Constants ( $a_{\text{N}\mu}$  and  $a_{\text{H}\mu}$  in G) for the Radical Ions of Cycl[3.3.3]azine ( $4\cdot^+$  and  $4\cdot^-$ ) and Its 1,3-Dicyano ( $4\mathbf{a}\cdot^+$  and  $4\mathbf{a}\cdot^-$ ) and 1,3-Di-*tert*-butoxycarbonyl Derivatives ( $4\mathbf{b}\cdot^+$  and  $4\mathbf{b}\cdot^-$ )

Position $\mu$		Radical cations			Radical anions		
		$4\cdot^+$	$4\mathbf{b}\cdot^+$	$4\mathbf{a}\cdot^+$	$4\cdot^-$	$4\mathbf{b}\cdot^-$	$4\mathbf{a}\cdot^-$
4,6,7,9	$a_{\text{H}\mu}$	(-) $6.45^a$	$5.63^b$	$5.39^b$	(+) $0.05^a$	$0.48^b$	$0.47^b$
2,5,8	$a_{\text{H}\mu}$	(+) $1.78^a$	$1.66^b$	$1.60^b$	(-) $4.84^a$	$5.09^b$	$5.22^b$
10	$a_{\text{N}\mu}$	(+) $1.29^a$	$1.19$	$1.01$	(+) $6.54^a$	$6.17$	$5.96$

<sup>a</sup> Sign required by theory. <sup>b</sup> Averaged values.

heteroatom parameters are required for semiempirical MO models of the substituted cycl[3.3.3]azines, the predictive potential of such models is substantially impaired. The discussion of the esr data for the pertinent radical ions will thus be restricted to qualitative remarks concerning the effect of substitution on the  $\pi$ -spin populations in  $4\cdot^+$  and  $4\cdot^-$ . Inspection of Table V, in which the coupling constants for  $4\cdot^+$  and  $4\cdot^-$  are compared with the corresponding values for the 1,3-disubstituted radical cations ( $4\mathbf{a}\cdot^+$  and  $4\mathbf{b}\cdot^-$ ), and anions ( $4\mathbf{a}\cdot^-$  and  $4\mathbf{b}\cdot^-$ ), suggests the following comments.

(1) For the radical cations, both the  $^{14}\text{N}$  and the averaged proton coupling constants *decrease* in magnitude on substitution, the effect being particularly pronounced for the large  $a_{\text{H}\mu}$  values ( $\mu = 1,3,4,6,7,9$ ). This finding indicates a *partial delocalization* of the  $\pi$ -spin population onto the substituents. In the case of  $4\mathbf{a}\cdot^-$ , such a delocalization is also evidenced by an additional coupling constant (0.82 G) observed for the  $^{14}\text{N}$  nuclei in the cyano group. Furthermore, the significant increase of the  $g$  values on substitution points in the same direction (see Results).

(2) For the radical anions, the averaged proton coupling constants *increase* in magnitude on substitution, whereas an *opposite* effect is exhibited by the  $a_{\text{N}\mu}$  values. This result can be interpreted as a *redistribution* of the  $\pi$ -spin population in the cycl[3.3.3]azine system with-

out a substantial delocalization onto the substituents. It is in line with the absence of the hyperfine splittings arising from the  $^{14}\text{N}$  nuclei of the cyano group in  $4\mathbf{a}\cdot^-$  and with the nearly invariant  $g$  value for all radical anions.

(3) The effect of substitution on the  $a_{\text{H}\mu}$  and  $a_{\text{N}\mu}$  values is uniformly larger for the dicyano than for the di-*tert*-butoxycarbonyl ester substitution.

The postulated changes in  $\pi$ -spin distributions upon the introduction of substituent groups in 1,3 positions of cycl[3.3.3]azine (**4**) can be readily rationalized with the aid of the MO models considered above. Since the HOMO  $\psi_A$  of **4** has large LCAO coefficients at the  $\pi$  centers 1,3 (Figure 4) and the corresponding  $\pi$ -spin populations  $\rho_\mu$  in  $4\cdot^+$  are high (Table II), an appreciable spin delocalization should occur on passing from  $4\cdot^+$  to  $4\mathbf{b}\cdot^+$  and  $4\mathbf{a}\cdot^+$ . In contrast, the LUMO  $\psi_S'$  of **4** exhibits very small coefficients at these centers (they are zero for the perimeter orbital  $\psi_S$  in Figure 4), and the  $\pi$ -spin populations  $\rho_\mu$  at  $\mu = 1,3$  in  $4\cdot^-$  nearly vanish (Table II). No substantial spin delocalization is therefore expected along the series  $4\cdot^-$ ,  $4\mathbf{b}\cdot^-$ , and  $4\mathbf{a}\cdot^-$ .

**Acknowledgments.** We thank Dr. B. Kowert for carrying out some preliminary experiments and reading the manuscript. This work was supported by the Schweizerische National Fonds (Project No. SR 2.477.71).