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GAIN IN MAGNETIC SHIELDING OF THE ^{15}N NUCLEUS IN A SUCCESSIVE SERIES OF RELATED 10, 12, AND 14 π-ELECTRON HETEROCYCLES: 2,1,3-BENZOTHIADIAZOLE, 1,3,2,4-BENZODITHIADIAZINE, AND 1,3,5,2,4-BENZOTRITHIADIAZINE*

M. M. Shakirov, I. V. Beregovaya, and A. V. Zibarev

A significant (~85 ppm) increase in shielding of the ^{15}N nucleus is observed in the successive series of 10, 12, and 14 π-electron heterocycles: 2,1,3-benzothiadiazole, 1,3,2,4-benzodithiadiazine, and 1,3,5,2,4-benzotrithiadiazine, as compared to the gain from both the full and the π-charge of the nitrogen atom. Possible antiaromaticity of the 12 π-electron dithiadiazine, containing a low-lying activation state, does not appear clearly in the ^{15}N NMR.

The ready development of the chemistry of π-excessive sulfur–nitrogen heterocycles in earlier times [2, 3] resulted in a series of nontrivial results. In particular, 1,3,2,4-benzodithiadiazine and its 5,6,7,8-tetrafluoro derivative (IIa, b; Scheme I) with a remarkable combination of some formal signs of antiaromaticity (planar geometry, 12 π-electron system) with thermodynamic stability were recently synthesized [4-8]. In distinction to the closely-related 10 π-electron 2,1,3-benzothiadiazole and the 14 π-electron 1,3,5,2,4-benzotrithiadiazepine (Ia, b and III, respectively, see Scheme I), the compounds IIa, b possess low-lying excitation states (see Table 1) which also can often be considered as attributes of antiaromaticity [9]. The possible antiaromaticity of compound IIa contrasts with the increased shielding of the H^5 and the H^8 nuclei in the H^1 NMR (δ 1H 5.70 and 5.50 ppm) [4], but in the ^{19}F NMR spectrum of compound IIb such features are absent [6].

In an extension of the study of heteroatom reaction rates [7] and the electronic structures [8] of compounds IIa, b, the present work studied their ^{15}N NMR spectra by comparison with the spectra of compounds Ia, b and III, as well as with some other related and model compounds (see Scheme I).

As indicated, in the series of thiadiazoles Ia(b)b, dithiadiazines IIa(b) and trithiadiazine III, the magnetic screening of the ^{15}N nucleus is significantly increased to ~85 ppm between its extreme members (see Table 1). Notably, a similar effect is observed in a series of acyclic analogs of I-III (compounds V-VII, see Scheme I), but on a significantly smaller scale and in a less distinct form (VI defaults, see Table 1); the latter may be caused by the fact that, in distinction from I-III, V-VII in sodium undergo complex isomeric equilibria (cf. for example, [10]).

It is well known that in a series of related compounds the change of $\delta^{15}N$ is connected, as a rule, with the change of average electron excitation energy ΔE and/or the effective charge on the N atom [11, 12]. From MNDO calculation data, I-III in fact increase in succession both as the full charge on the N atom q(N) and its π-charge $q\pi(N)$ (see Table 1), basically because of the mixing of the electron density with the sulfur atom, but a rigid correlation with $\delta^{15}N$ was not observed. Under these conditions, however, when the ^{15}N nucleus becomes part of a chromophore (compounds I-III), particularly one possessing

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*Part IX in the series "Cyclic Aryleneazachalcogenins." For Part VIII, cf. [1].

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TABLE 1. Spectral and Calculated Characteristics of Compounds I-VII*

Compound	Charge, e		$\delta^{15}N$, ppm	λ_{max}, nm, lg(ε)	
	$-q$(N)	$-q\pi$(N)		experimental	CNDO/S
I a	0,31	0,20	332,4	311 (4,15)	267 (4,13)
I b	0,28	0,18	306,6	326 (3,39)	—
II a	0,68 (N^2), 0,57 (N^4)	0,37 (N^2), 0,49 (N^4)	269,5, 263,5	617 (2,7)	646 (3,92)
II b	0,67 (N^2), 0,61 (N^4)	0,32 (N^2), 0,52 (N^4)	255,3, 233,1	615 (2,26)	653 (3,99)
III	0,86	0,50	248,8	384 (3,7)	380 (4,30)
IV	0,36	0,22	292,9	645 (2,70)	—
V	0,51 (N^Z), 0,60 (N^E)	0,34 (N^Z), 0,41 (N^E)	296,7	420 (4,07)	476 (4,91)
VI	0,66 (N^Z), 0,60 (N^E)	0,39 (N^Z), 0,46 (N^E)	328,7, 264,9	434 (4,15)	403 (3,37)
VII	0,79	0,47	277,5	450 (4,03)	404 (4,79)

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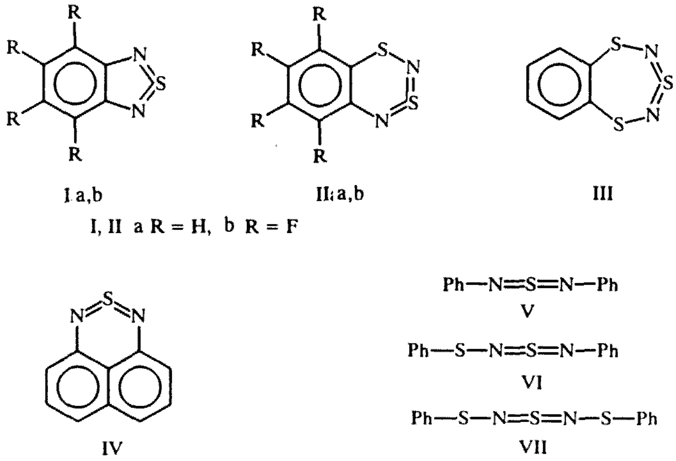
*For compounds IIa, IIb, III, IV, VI, and VII, the spectral data were obtained in the percent work, and the rest from the literature, ^{15}N NMR; Ia [19] (cf. $\delta^{14}N$ [20]), Ib [21], V ($\delta^{14}N$) [20], UV: Ia [22], IIa, [4], III [4], IV [22], V [23]. The coefficients used for conversion of $\delta^{15}N$ to NH_3; 20.68 from NH_4NO_3 (saturated aqueous solution), 375.80 from HNO_3 (1 M), 380.23 from $MeNO_2$ [24]. The value of $\delta^{15}N$ for V [19] was incorrect [25], whereas $\delta^{15}N$ for IV [19] agrees with that obtained in the present work. The isomeric equilibrium of V-VII in solution was neglected in the CNDO/S calculations; the configurations discovered in crystals [E, Z, E, Z, and Z, Z, respectively (cf. [10, 15] and works cited therein)] were used. For IV the CNDO/S significantly overestimates the λ_{max} (870 nm); PPP-Cl gives better results (733 [26] and even 661 nm [22]).

Scheme 1



I a,b

II a,b

III

I, II a R = H, b R = F

IV

Ph—N=S=N—Ph

V

Ph—S—N=S=N—Ph

VI

Ph—S—N=S=N—S—Ph

VII

a low-lying excitation state (compounds IIa, b), the most essential factor may be the change in ΔE [11, 12]. In the I-III series as well as in IV (an additional example of a 14π-electron thiadiazine; see Scheme I) having, as with IIa, b, a low-lying excitation state, any correlation with $\delta^{15}N/\lambda_{max}$ is absent (see Table 1), which, on the one hand, is typical for sulfur–nitrogen compounds [2, 11], and on the other, agrees with the results of calculations of the UV spectrum of these materials by the CNDO/S method (see Table 1), indicating the nonmagnetoactive [11] $\pi-\pi^*$ character of the corresponding electron excitation (for III this is independently supported by the results of a study of the magnetic circular dichroism spectrum [13]). Thus, the change of ΔE apparently does not contribute significantly to the discovered effect, and its basic cause is probably the above-noted shielding of the electron density around the nitrogen nucleus.

On the whole, it can be said that the formal possible antiaromaticity of compounds IIa, b is not clearly exhibited in the $\delta^{15}N$ NMR spectra. This agrees with the conclusion [8] that IIa, b are more similar to conjugated nonaromatic, than to traditional antiaromatic materials.

EXPERIMENTAL

Compounds IIa [4], IIb [6], III [4], IV [14], VI [15], and VII [16] were synthesized by known methods. Their ^{15}N NMR spectra were measured under natural isotope content with a Bruker AM-400 spectrometer and a frequency of 40.55 MHz in a 3:1 $CHCl_3/C_6D_6$ solution, external standard NH_3 (g); their UV spectra were determined in heptane solution. Data for the remaining compounds are from the literature (See Notes, Table 1).

MNDO calculations were conducted with complete optimization of geometry by the MNDO-89 program, an extension of program MNDO-85 [17, 18]. The CNDO/S calculations were completed with the NDOL program [18] for molecular geometry optimized by the MNDO method.

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