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Formation and Identification of Aryldiazenyl Radicals Using the ESR Technique[1]

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Aryldiazenyl radicals were formed at −104—−116 °C by photoirradiation of cyclopropane solutions of 1-aryl-2-(arylthio)diazenes and of 1-aryl-3,3-dimethyltriazenes in the presence or absence of olefins, and also by irradiation of cyclopropane solutions of substituted 1,2,3-benzothiadiazoles in the presence of di-*t*-butyl peroxide. The ESR spectra were analyzed and the hfs constants were assigned by reference to the spectra of methyl, ^{2}H, and ^{15}N-labelled aryldiazenyl radicals and to the results of CINDO calculations. Aryldiazenyl radicals are relatively persistent and the -N=N group rotates about the C-N^2 bond axis. The preferred conformations of the radicals were considered.

Aryldiazenyl radicals have been the subject of much interest in organic chemistry during the last decades.[2] The appearence of the radicals in transient states was suggested by chemical facts such as the formation of compounds derived from the aryldiazenyl radicals,[3,4] and of isomeric azo compounds.[5] The most conclusive evidence for the radicals was the isolation of phenylazotriphenylmethane in the thermolysis of α-(phenylazo)cumene in the presence of triphenylmethyl radicals.[6] Aryldiazenyl radicals have, however, not yet been directly characterized by any spectroscopic method, and the physical and chemical properties of the radicals have remained unclear. We report here on the detection and identification of aryldiazenyl radicals by the ESR method and on their possible conformations by reference to theoretical calculation of the hfs constants.

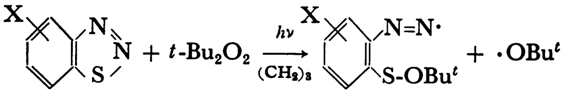
Results and Discussion

(1) Formation and Detection of Aryldiazenyl Radicals. Cyclopropane solutions of ortho-, meta-, and para-substituted 1-phenyl-2-(arylthio)diazenes were irradiated in the ESR cavity using a Xe lamp (1 kW) through a filter of 420 nm at −104—−116 °C to afford radicals which will be later identified as substituted phenyldiazenyl radicals (Reaction 1). From 1-(4-methylphenyl)- and 1-(4-methoxyphenyl)-3,3-dimethyltriazenes we obtained radicals with the same constitution as those from diazenes, more conveniently by using a N$_2$ Laser (Molectron UV-14) than by using a Xe lamp (Reaction 2). Starting with 1-(4-dimethylaminophenyl)-3,3-dimethyltriazene we could not observe the ESR spectrum of the corresponding radicals, because of its poor solubility in cyclopropane at low temperatures. From these two kinds of starting compounds we obtained the spectra of the same nitrogen-centered radicals. This confirmed that the radicals we observed were indeed the primary radicals formed by the photolysis of diazenes and triazenes, and not the radicals formed secondarily by any radical addition reaction to diazenes or triazenes. This conclusion was further supported by experiments using neat or mixed solvents of olefins and cyclopropane for 1-aryl-2-(arylthio)diazenes: Olefinic solvents such as 1-butene, *cis*-2-butene, and propene did not cause any change in the ESR spectra observed (Reaction 1). Olefinic solvents caused some acceleration in the decay rate of the aryldiazenyl radicals, on which we will reported in the next paper.

The third type of starting compounds for the nitrogen-centered radicals of the same sort were substituted 1,2,3-benzothiadiazoles, whose thiadiazole rings were opened photochemically by using di-*t*-butyl peroxide (Reaction 3).

$$\underset{(\mathrm{R=H,\ 4\text{-}Bu}^t)}{\mathrm{Ar\text{-}N{=}N\text{-}S\text{-}C_6H_4\text{-}R}} \xrightarrow[(\mathrm{CH_2})_3+\mathrm{R^1CH{=}CHR^2}]{h\nu} \mathrm{Ar\text{-}N^2{=}N^1\cdot} + \mathrm{\cdot S\text{-}C_6H_4\text{-}R} \qquad (1)$$

$$\mathrm{Ar\text{-}N{=}N\text{-}N(CH_3)_2} \xrightarrow[(\mathrm{CH_2})_3]{h\nu} \mathrm{Ar\text{-}N{=}N\cdot} + \mathrm{\cdot N(CH_3)_2} \qquad (2)$$



(3)

The hyperfine splitting constants of the radicals observed during these reactions together with *g*-values are listed in Table 1.

Photolysis of 1-(4-*t*-butylphenylthio)-2-phenyldiazene (No. 9) gave an ESR spectrum of nine 1:2:1 triplets (1.2 G†) in a pattern of 1:1:1 triplet (22.5 G) of 1:1:1 triplets (9.45 G). This pattern of triplet of triplets, together with the low *g*-value of 2.0002, is the characteristic feature of the spectra of all the radicals we observed in the reactions 1, 2, and 3. In the following, we are going to identify them as aryldiazenyl radicals by examining the reactions of their formation and by analyzing the ESR spectra.

(2) Identification of the Aryldiazenyl Radicals. The pattern of triplet (1:1:1) of triplets (1:1:1) characteristic of the ESR spectra obtained in this work, shows that the

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† 1 G=1×10^{-4} T.

Table 1. Hyperfine Splitting Constants of Aryldiazenyl Radicals[a)] $Ar-N^2=N^1\cdot$

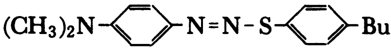
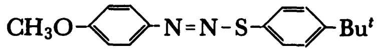
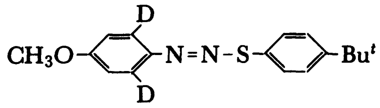
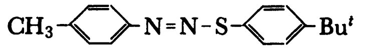
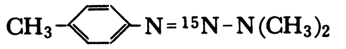
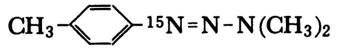
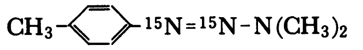
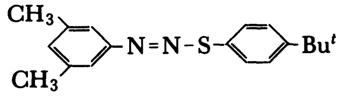
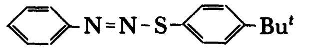
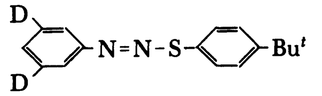
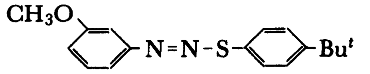
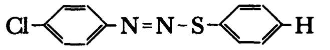
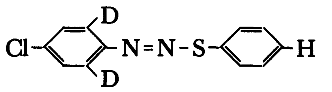
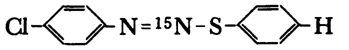
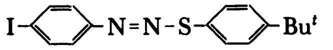
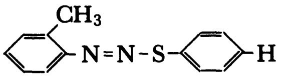
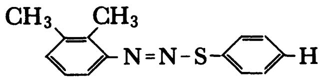
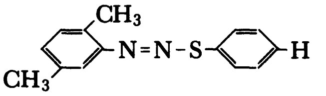
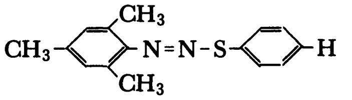
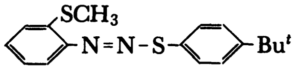
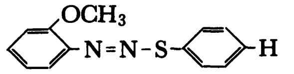
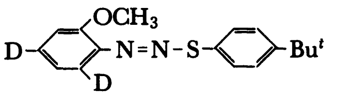
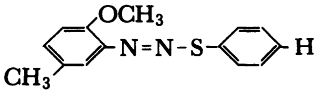
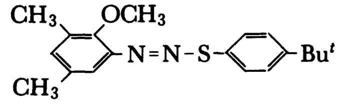
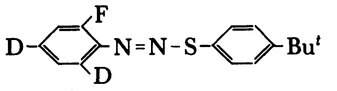
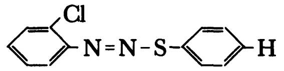
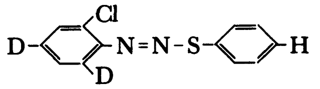
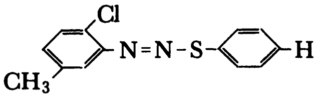
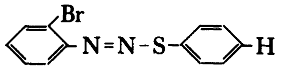
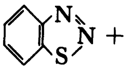
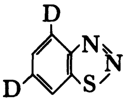
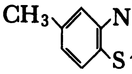
No.	Starting Compound of Ar-N=N·	g-Value (±0.0001)	Hfs. Const./G[b)]			(x-H)[c)]
			a_{N^1}	a_{N^2}	a_H	
1		2.0005	9.4_6	22.0	1.0_0	(3,5-H)
2		2.0004	9.6_0	22.4	1.0_6	(3,5-H)
3		2.0004	9.4_8	22.5	1.1_0	(3,5-H)
4		2.0004	9.3_5	22.7	1.1_0	(3,5-H)
5		2.0004	13.4_5	23.0	1.1_5	(3,5-H)
6		2.0003	9.6_5	31.6	1.1_5	(3,5-H)
7		2.0002	13.3_0	31.4	1.2_0	(3,5-H)
8		2.0003	9.4_5	22.7	None	
9		2.0002	9.4_5	22.5	1.2_0	(3,5-H)
10		2.0003	9.4_5	22.9	None	
11		2.0004	9.5_0	22.8	1.1_5	(5-H)
12		2.0003	9.1_3	22.8	1.2_0	(3,5-H)
13		2.0004	9.3_5	23.1	1.0_0	(3,5-H)
14		2.0002	13.3_0	23.0	1.1_0	(3,5-H)
15		2.0006	9.4_8	23.0	1.0_4	(3,5-H)
16		2.0002	9.5_0	23.0	1.8_5	(5-H)
17		2.0003	9.2_5	23.1	2.0_0 0.4_7	(5-H) (6-H)
18		2.0003	9.3_5	22.8	None	
19		2.0001	9.7_0	22.0	0.7_5	(2,6-Me-H)
20		2.0004	9.4_0	22.8	1.2_2 0.7_0	(5-H) (3-H)
21		2.0005	9.7_5	24.5	1.3_0 0.5_0	(5-H) (3-H)
22		2.0003	9.6_0	24.3	1.3_5 0.6_0	(5-H) (3-H)
23		2.0002	9.7_5	24.5	0.5_3	(3-H)

Table 1. (Continued)

No.	Starting Compound of Ar–N=N·	g-Value (±0.0001)	Hfs. Const./G[b)] a_{N^1}	a_{N^2}	a_H	(x–H)[c)]
24		2.0004	9.5_8	22.8	None	
25		2.0003	9.6_0	25.7	0.9_6 0.4_8	(5-H) (3-H) a_F: 1.4_4
26		2.0006	9.3_8	25.3	1.6_5	(5-H)
27		2.0008	9.3_5	25.4	1.7_4	(5-H)
28		2.0007	9.6_0	25.5	None	
29		2.0024	9.4_5	25.6	1.9_0	(5-H)
30	 + t-Bu_2O_2	2.0002	9.3_2	20.9	1.3_2	(3-H)
31	 + t-Bu_2O_2	2.0002	9.3_5	20.8	1.3_0	(3-H)
32	 + t-Bu_2O_2	2.0002	9.2_0	21.0	1.3_4	(3-H)

a) The ESR spectra of (perdeuterio-, 2-F-, 4-Br-, 3- and 4-$CH_3C(O)$-, 3- and 4-NC-, 4-$CH_3OC(O)$-, and 5-CH_3-2-CH_3S-phenyl)diazenyl radicals showed the same pattern as those in Table 1 and the spectra were in accordance with the discussions in this report. b) 1 Gauss=1×10^{-4} T. c) x denotes the position of the hydrogen atom on the benzene ring which gives rise to the hfs constant a_H.

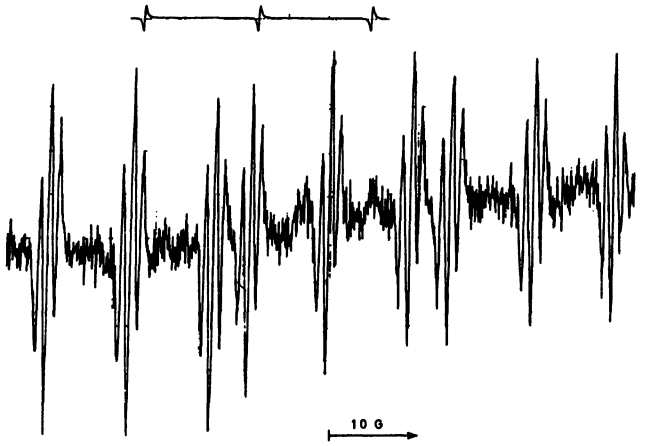


Fig. 1. ESR spectrum of (4-chloro-2,6-dideuteriophenyl)-diazenyl radical.

Fig. 2. ESR spectrum of (3-methoxyphenyl)diazenyl radical.

unpaired electron is coupled to two ^{14}N nuclei. This is further proved by the specific ^{15}N-labelling discussed below. The large splitting constants point to nitrogen centered radicals as expected for aryldiazenyls.

The additional small coupling of 0.5 to 2.0 G must then be ascribed to at least some of the aryl ring protons. In order to identify these protons, we compared the ESR spectra of specifically substituted or deuterated species.

Substitution of hydrogen-4 of the phenyl group by methoxyl (from No. 9 to No. 2) and by chlorine (No. 12), and further substitution of hydrogen-2 and -6 by deuterium (Nos. 3 and 13) did not cause any change of the 1:2:1 triplets, attributed to hydrogen hfs. (Fig. 1) In the case of 1-(4-t-butylphenylthio)-2-(3-methoxyphenyl)diazene (No. 11) the spectrum pattern was, however, converted into nine doublets (1.15 G). (Fig. 2)

1-(4-t-Butylphenylthio)-2-(3,5-dimethylphenyl)diazene (No. 8, Fig. 3) and 1-(4-t-butylphenylthio)-2-(3,5-dideuteriophenyl)diazene (No. 10) both gave nine singlets

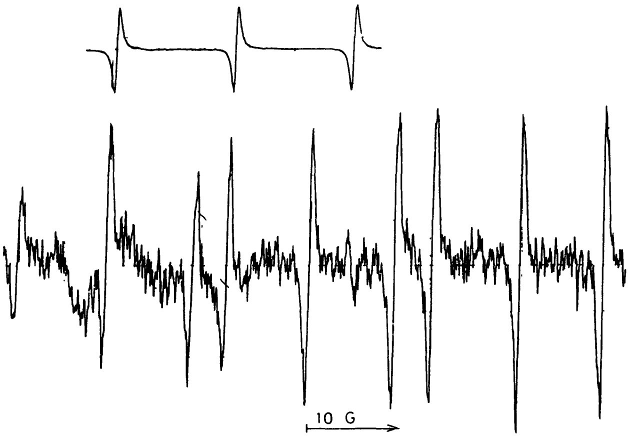


Fig. 3. ESR spectrum of (3,5-dimethylphenyl)diazenyl radical.

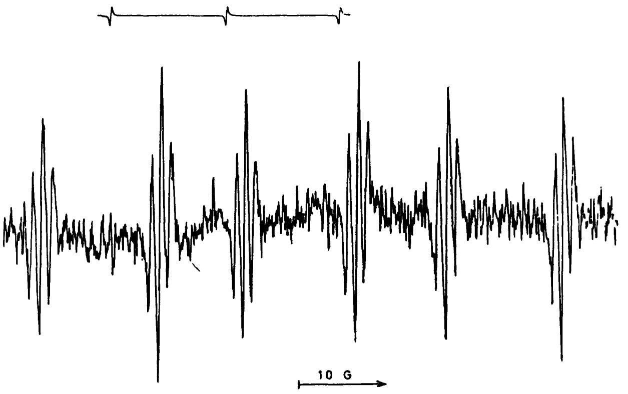


Fig. 4. ESR spectrum of (4-chlorophenyl)diazenyl-1-^{15}N radical.

in a pattern of 1:1:1 triplet (22.7 and 22.9 G, respectively) of 1:1:1 triplets (9.45 and 9.45 G, respectively). The successive disappearence of the hydrogen hfs from No. 9 to 11 to Nos. 8 and 10 proves that the hfs results from the meta hydrogens of the aryl group.

When 2-^{14}N of 1-(4-chlorophenyl)-2-(phenylthio)diazene was replaced by ^{15}N via diazotization of chloroaniline using sodium nitrite- ^{15}N in the preparation of the diazene, the pattern of the ESR spectrum of the nitrogen nuclei changed from a triplet of triplets into a triplet of doublets: 1-(4-Chlorophenyl)-2-(phenylthio)diazene-2-^{15}N (No. 14) gave a spectrum composed of six 1:2:1 triplets (1.1 G) in an arrangement of 1:1:1 triplet (23.0 G) of doublets (13.3 G, Fig. 4).

A similar change in the spectrum pattern due to the nitrogen isotope was observed in the experiments using ^{15}N-triazenes. If 2-^{14}N of 1-(4-methylphenyl)-3,3-dimethyltriazene was replaced by ^{15}N (No. 5), then the spectrum pattern (triplet of triplets as in the case of No. 4) changed into a 1:1:1 triplet (23.0 G) of doublets (13.45 G, Fig. 5). If on the other hand the 1-^{14}N of the original triazene was replaced by ^{15}N (No. 6), then it gave a spectrum of a doublet (31.6 G) of 1:1:1 triplets (9.65 G, Fig. 6). Triazene-1,2-$^{15}N_2$ (No. 7) gave a spectrum of a doublet (31.4 G) of doublets (13.3 G, Fig. 7).

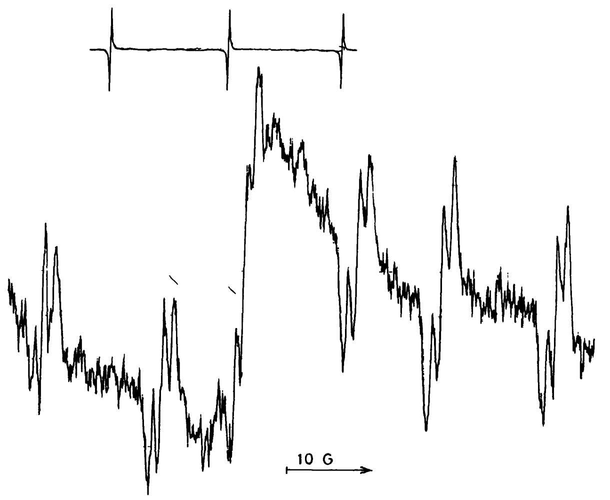


Fig. 5. ESR spectrum of (4-methylphenyl)diazenyl-1-^{15}N radical.

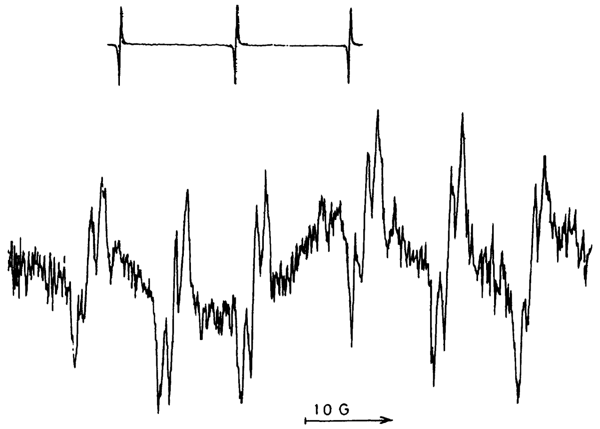


Fig. 6. ESR spectrum of (4-methylphenyl)diazenyl-2-^{15}N radical.

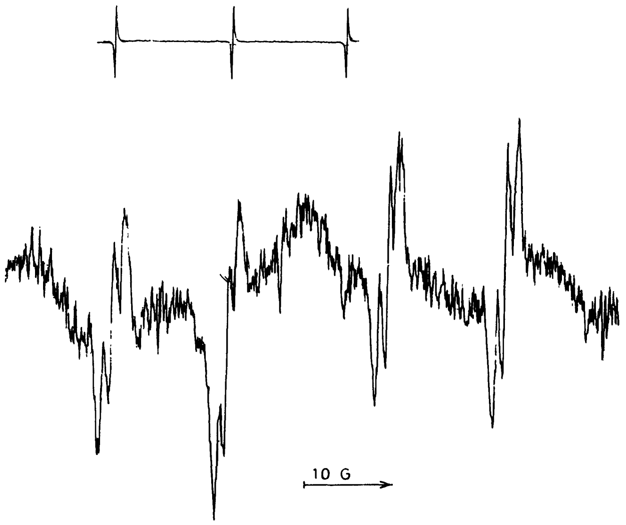


Fig. 7. ESR spectrum of (4-methylphenyl)diazenyl-1,2-$^{15}N_2$ radical.

In every case, the small triplet splitting (1.1—1.2 G), attributed to the meta ring protons, was also resolved. The ratios, 13.4 G/9.7 G and 31.5 G/23.0 G, are in good accordance with the magnetogyric ratio of $|^{15}N/^{14}N|=1.40$. These results assigned the hfs constants of 23.0 G to 2-^{14}N and that of 9.7 G to 1-^{14}N of the aryldiazenyl radical structure.

The *g*-values of these nitrogen centered radicals were low, 2.0003 on the average, except for the *g*-value of (2-bromophenyl)diazenyl, 2.0024 (No. 29, see below). These values are lower than those of carbon radicals such as triphenylmethyl radical (2.00266[7]), aminyl radicals such as *N*-aryl-*t*-butylaminyls (2.0035[8]), and thiyl radicals derived from cysteine (2.025[9]). They are, however, very close to those of 2-butenoyl radicals, 2.0005,[10] to those of nitrosobenzene cation radicals, 2.0007,[11] and to those of benzoyl radicals, 2.0014.[12] The latter three radicals are reported to be σ-radicals.

From these remarkable ESR features (large nitrogen hfs, small *meta*-ring proton hfs, low *g*-values) we may draw two conclusions: (i) The data exclude the possibility of the radicals being some kind of *N*-centered radicals such as 2-substituted 2-(arylthio)-1-phenylhydrazyl, $Ar{-}S{-}N(X){-}\dot{N}{-}C_6H_5$, because the hydrazyl radicals should have a *g*-value of about 2.0035, as high as that of phenylaminyl radicals.[8] Moreover, phenylaminyl radicals are π-radicals and afford measurable hfs constants of ortho and para hydrogens of the aryl ring, which is, however, not the case with the present radicals. The possibility that they are 2-substituted 1-(arylthio)-2-phenylhydrazyl radicals, $C_6H_5{-}N(X){-}\dot{N}{-}S{-}Ar$, is also very small, because arylthioaminyl radicals should have a *g*-value of ca. 2.006,[13] a high value due to the conjugation of the nitrogen radical center with the arylthio group. Arylthioaminyl radicals should also give appreciable hfs constants of ortho and para hydrogens of the arylthio group, which in our case was not detected, on substitution of the 4-*t*-butyl group by hydrogen.

The assignment of the structure of hydrazyl radicals as those cited above to our nitrogen centered radicals can also be excluded if we consider the reaction conditions of radical formation in olefinic solvents, Reaction 1. Finally, such radicals should not be formed from triazenes, Reaction 2. (ii) The low *g*-values of the aryldiazenyl radicals can be explained by assuming a σ-radical structure.

The relatively high *g*-value of 2.0024 for the (2-bromophenyl)diazenyl (No. 29), contrary to the *g*-value of 2.0006 for the (4-iodophenyl)diazenyl radical (No. 15), is remarkable. The very small increase in the *g*-value for the (4-iodophenyl)diazenyl, (as compared to Nos. 9 and 12), thus gives evidence for a very small spin density at the 4-position of the phenyl group because of the σ-radical nature. The *g*-value of 2.0024 of (2-bromophenyl)diazenyl may also be an indication of a through-space interaction between bromine and the radical center. (2-Chlorophenyl)diazenyl radicals (Nos. 26—28) showed a much smaller increase in *g*-values, to ca. 2.0007. From 1-(4-*t*-butylphenylthio)-2-(2-iodophenyl)diazene we could not observe any definitely interpretable spectrum.

Phenyldiazenyl radical (No. 9), as already mentioned, revealed hfs due to the meta hydrogens, and not to the ortho and para hydrogens. Furthermore, methyl substitution for the meta hydrogens completely suppressed the original hydrogen hfs (No. 8). This fact is not generally true for π-radicals, and also gives support for the σ-radical nature of aryldiazenyl radicals.

(2,4,6-Trimethylphenyl)diazenyl radical (No. 19), on the other hand, revealed a hydrogen hfs which was ascribed to the protons of the ortho methyl groups. A similar methyl-hydrogen hfs was reported for 2,4,6-trimethylbenzenesulfonyl radicals.[14] (See discussion on page 1883.) Based on the chemical methods of formation, Reactions 1—3, and on the analysis of the ESR spectra observed, we concluded that the radicals obtained were aryldiazenyl σ-radicals.

Apparently, two groups of *ortho*-substituted phenyldiazenyl radicals exist, as based on the hydrogen hfs analysis: 1) (2-Substituted phenyl)diazenyl radicals showing two different hfs constants of the meta hydrogens, to which (2-fluoro-, 2-methoxy-, and 2-methylthiophenyl)diazenyl radicals belong, and 2) (2-substituted phenyl)diazenyl radicals revealing only one hydrogen hfs constant of hydrogen-5, to which (2-methyl-, 2-chloro-, and 2-bromophenyl)diazenyl radicals belong.

(2-Methoxyphenyl)diazenyl radical of group 1) showed hfs constants of 0.50 G for hydrogen-3 and of 1.30 G for hydrogen-5, and the assignment was confirmed by experiments Nos. 22—24. The hfs constants of (2-fluoro- and 2-methylthiophenyl)diazenyl radicals were assigned in analogy to (2-methoxyphenyl)diazenyl radical ($a_{H-5}>a_{H-3}$) and partly supported by experiments.*) In the case of (2-fluorophenyl)diazenyl, the highest non-nitrogen hfs constant observed was attributed to fluorine, based on the calculated values.

(2-Methyl- and 2-chlorophenyl)diazenyl radicals of group 2) revealed only one hydrogen hfs constant each, 1.85 and 1.65 G, respectively (Nos. 16 and 26), and the assignments were based on the experiments Nos. 18 and 28. The hydrogen hfs of (2-bromophenyl)diazenyl radical was assigned to hydrogen-5 in analogy to (2-chlorophenyl)diazenyl radical. Hydrogen hfs constants of some representative aryldiazenyl radicals are reproduced in Fig. 8.

(3) Possible Conformations of Aryldiazenyl Radicals. a) A Model of Rotation of the N=N Group about the C–N^2 Bond Axis, with a Preference of Staying in a Position out of the Plane of the Benzene Ring: Phenyldiazenyl radicals are very similar to benzoyl radicals, as regards σ-radical character and hydrogen hfs. In order to obtain a qualitative picture

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*) (2-Fluorophenyl)diazenyl radical gave the same ESR spectrum as that of (2-fluoro-4,6-dideuteriophenyl)diazenyl (No. 25). The assignment of 1.22 G to hydrogen-5 for (2-methylthiophenyl)diazenyl was supported by comparison with (5-methyl-2-methylthiophenyl)diazenyl radical (*g*=2.0002, a_{H-3}=0.50 G).

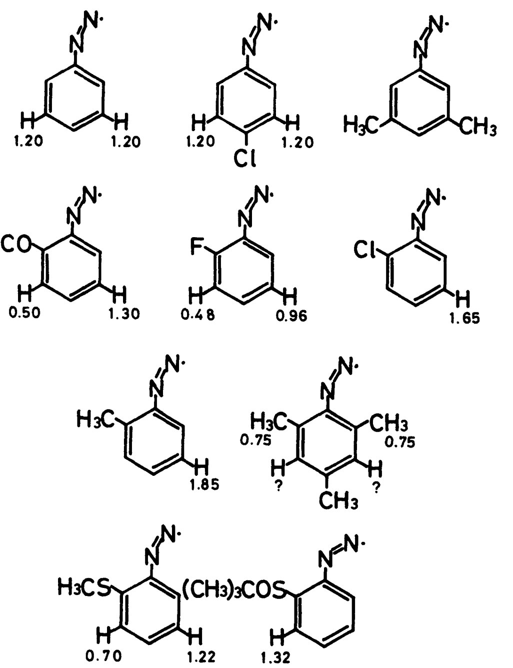

Fig. 8. Hyperfine splitting constants of aryldiazenyl radicals.

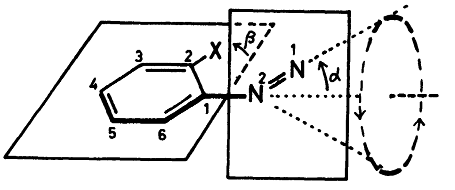

Fig. 9. Conformation of aryldiazenyl radicals with rotating N=N group about the C–N^2 bond axis. X stands for the substituent group.

of the conformation of aryldiazenyl radicals we performed INDO calculations[15] on phenyldiazenyl radical and on (2-fluoro-, 2-methyl-, 2-methoxy-, and 2,6-dimethylphenyl)diazenyl radicals. These calculations suggested that phenyldiazenyl radicals have conformations in which the azo group rotates about the C–N^2 bond axis with a preference in the "vertical" form: The N^1 atom of the radical is raised out of the plane of the benzene ring, forming an angle between the bonds C–N^2 and ^{1}N–N^2 (angle α, Fig. 9) of 40°, and an angle between the plane of the benzene ring and the plane C–N^2–N^1 (angle β) of 90°.

In the INDO calculations we have, first of all, searched for a conformation of the minimum total energy, and it was the vertical form for phenyldiazenyl radical with the total energy (T.E.)=−67.017750 a.u. The calculated highest hfs constants 0.80 G, of hydrogen-3 and -5 for this vertical conformation were in fairly good agreement with the symmetric spin distribution observed in the ESR experiments ($a_{H-3}=a_{H-5}=1.20$ G).

The molecular dimensions in the vertical form were as follows: Normal benzene ring; C–N^2=1.40 Å; N^1–N^2=1.20 Å; the angle α=40°, and the angle β=90°. The bond length C–N^2 used in the calculations was that of azobenzene,[16] but the length N^1–N^2 was shortened by 0.03 Å from that of azobenzene. The angle α was decreased from 60° of azobenzene to 40°.

Table 2. Hyperfine Splitting Constants of Phenyldiazenyl Radical, Calculated by INDO Method[a] (Gauss)[b]

Ph–N^2=$N^1\cdot$

β=	a_{N^1}	a_{N^2}	$a_{2\text{-H}}$	$a_{3\text{-H}}$	$a_{4\text{-H}}$	$a_{5\text{-H}}$	$a_{6\text{-H}}$
0°	5.07	20.33	0.27	1.70	0.21	−0.33	1.76
10	5.10	20.04	0.24	1.66	0.15	−0.27	1.67
20	5.13	19.43	0.18	1.59	0.01	−0.13	1.45
30	5.18	18.78	0.15	1.48	−0.13	0.03	1.24
40	5.24	18.16	0.16	1.37	−0.25	0.17	1.06
50	5.30	17.61	0.20	1.24	−0.34	0.31	0.90
60	5.35	17.17	0.26	1.13	−0.41	0.44	0.78
70	5.39	16.85	0.33	1.01	−0.46	0.56	0.67
80	5.40	16.72	0.40	0.91	−0.49	0.69	0.56
90	5.41	16.64	0.48	0.80	−0.50	0.80	0.48
found	9.45	22.5	—	1.20	—	1.20	—

a) Calculation was performed using α=40°, C–N^2=1.40 Å, and N^1–N^2=1.20 Å. b) 1 Gauss=1×10^{-4}T.

Similar calculations by this method were also reported by Kasukhin and others for phenyldiazenyl radicals with a planar conformation,[17a)] and by Seifert and Gerhart on a vertical conformation.[17b)] Our results of INDO calculations for the vertical form affording the highest hfs constant for the hydrogen-3 and -5 differed from those of Seifert and Gerhart[17b)] which revealed the highest hfs constants for 2,6-hydrogens. This difference is probably due to the different molecular dimensions used by these authors.

The calculation on a planar form with the same molecular dimensions except for β=0°, yielded a total energy higher than that of the vertical form by 4.17 kcal/mol†, and an asymmetric spin distribution over the aromatic hydrogens, as was reported by Kasukhin and others[17a)] (Table 2). Since the difference between the total energies of the vertical and planar conformations was rather low, it is plausible to assume that the azo group of the phenyldiazenyl radical rotates about the C–N^2 bond axis with a high probability that it stays in the vertical form.

By using the bond lengths of phenyldiazenyl radical, we also calculated the hfs constants for the planar conformations of (2-fluoro-, 2-methyl-, 2-methoxy-, and 2,6-dimethylphenyl)diazenyl radicals with a smaller extent of variation of α. It turned out that the angle α=40° characterized the most stable planar conformation for all aryldiazenyl radicals considered. The vertical form of these aryldiazenyl radicals were found to be more stable by 2 to 4 kcal/mol than the corresponding planar conformations.

To a first approximation, these minima in T. E. sug-

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† 1 cal=4.184 J.

Table 3. Hyperfine Splitting Constants of 2-Substituted Phenyldiazenyl Radicals Found and Calculated by the INDO Method and the Difference in Total Energy between Conformations[a)]

2-Substituent in Ar–N=N·	found / calcd	β°	a_{N^1}	a_{N^2}	$a_{3\text{-H}}$	$a_{4\text{-H}}$	$a_{5\text{-H}}$	$a_{6\text{-H}}$	a_X	T.E.[c)] kcal[d)]/mol
			Gauss[b)]							
2-F	f.	—	9.60	25.7	0.48	—	0.96	—	a_F: 1.44	
	c.	90	5.25	18.02	1.00	−0.57	0.79	0.63	6.78	−3.61
	c.[e)]	110	5.32	18.27	0.73	−0.51	1.00	0.48	7.01	−3.29
2-CH_3O	f.	—	9.75	24.5	0.50	—	1.30	—	—	
	c.	90	5.31	17.84	1.02	−0.53	0.82	0.55	—	−2.82
	c.[e)]	120	5.25	18.38	0.58	−0.42	1.16	0.33	—	−2.19
2-CH_3	f.	—	9.50	23.2	—	—	1.85	—	—	
	c.	90	5.40	16.59	0.74	−0.48	0.84	0.37	$a_{Me\text{-}H}$: 0.67	−3.99
	c.[e)]	150	5.18	18.67	0.01	−0.21	1.54	0.09	0.14	−1.11
2,4,6-$(CH_3)_3$	f.	—	9.70	22.0	?	—	?	—	$a_{Me\text{-}H}$: 0.75	
2,6-$(CH_3)_2$	c.[e)]	90	5.39	16.57	0.78	−0.46	0.78	—	0.68	−2.51

a) The molecular dimensions for the calculations were $\alpha=40°$, C–N^2=1.40 Å, and N^1–N^1=1.20 Å. b) 1 Gauss=1×10^{-4} T. c) The difference in total energies: $\text{T.E.}_\beta-\text{T.E.}_{\beta=0°}$. d) 1 cal=4.184 J. e) The angle β which gave the best fit of calculated hyperfine splitting constants to the experimental data.

gest that for aryldiazenyl radicals carrying 2-fluoro, 2-methyl, 2-methoxy-, and 2,6-dimethyl substituents, the N=N group rotates about the C–N^2 bond axis. A best fit of the calculated hydrogen hfs constants and the experimental data was, however, not found in the conformation with β=90° but in a certain nonplanar form except for (2,6-dimethylphenyl)diazenyl radical (Table 3). We are not going into further discussion on the conformations of the aryldiazenyl radicals, because of the limited accuracy of our calculations. In any case, it is plausible to assume a rotation of the N=N group with energy barriers of several kcal/mol, with a preference of a certain specified conformation.

In benzoyl radical[12] and in benzenesulfonyl radicals,[14] the groups C=O and SO_2 were reported to rotate about the bond connecting them to the benzene ring. Nitrosobenzene cation radical was presumed to be in a specified conformation, holding the oxygen atom above the plane of the benzene ring at an angle β of ca. 70°.[11]

The (2,4,6-trimethylphenyl)diazenyl radical revealed a hfs of nine septes (0.75 G). This suggested a symmetrical spin distribution on the six ortho methyl hydrogens. The INDO calculations for (2,6-dimethylphenyl)diazenyl in the vertical conformation gave hfs constants of 0.68 G for the ortho methyl hydrogens and 0.78 G for the 3,5-hydrogens. Thus, the observed proton hfs may also be of the nonet type, with two signals disappearing in the wings of the spectrum due to low intensity. At present, we cannot finally decide between a septet or a nonet structure.

We do not know why (2-methylphenyl)diazenyl radical (No. 16) gave a doublet and (2-methoxyphenyl)diazenyl (No. 21) a double doublets structure of the proton hfs. Comparison of the calculated hydrogen-3 hfs constants of these radicals in the vertical form may give some indication. The constant of (2-methoxyphenyl)diazenyl, 1.02 G, was higher than that of (2-methylphenyl)diazenyl, 0.74 G, and this higher value might lead to the experimantally observed hfs of hydrogen-3 in the methoxy compound. We could not ascribe these differences simply to the electronegativity of the substituents.

b) A Model of Planar Conformation with N^1 in the Side Opposite to the 2-Substituent, Maintaining a High Angle α: The ESR experiments Nos. 30—32 suggested that the hfs constant of (2-*t*-butoxythiophenyl)diazenyl radical resulted from hydrogen-3. In order to gain insight into this exceptional hfs, we carried out CNDO calculations on (2-methylthiophenyl)diazenyl radical as a model by varying the angle α from +80° to −80° for the planar conformations (β=0°), and also by varying α for the vertical forms (β=90°). Although the agreement of the calculated hfs constants with the experimental ones was very poor, the best fit of the hydrogen hfs in the case of (2-*t*-butoxythiophenyl)diazenyl radical was found in the conformation with α=−80° in a planar form. The results of calculations for the vertical forms were completely unsatisfactory. It is of significance here to see that the INDO calculation for the planar conformation of (2-methylphenyl)diazenyl radical with α=−80° afforded the highest hydrogen hfs constant for hydrogen-3.*)

The angle of α=−80° may be understood, if one assumes that the ring opening of the thiadiazole by the attack of a *t*-butoxyl radical on the sulfur atom is followed by the rotation of the azo group about the C–N^2 bond axis by 180° to the opposite side of the 2-*t*-butoxythio substituent, and that the repulsion between the substituent and the lone pair electrons of N^2 is very high.

Experimental

(1) Syntheses of 1-Aryl-2-(arylthio)diazenes. 1-Aryl-2-

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*) The calculation on (2-methylphenyl)diazenyl radical using α=−80°, β=0°, C–N^2=1.42 Å, and N^1–N^2=1.20 Å, gave a_{N1}=7.89 G, a_{N2}=8.30 G, $a_{3\text{-H}}$=0.99 G, $a_{4\text{-H}}$=0.49 G, $a_{5\text{-H}}$=−0.15 G, and $a_{6\text{-H}}$=−0.09 G.

(arylthio)diazenes were prepared according to the method of Zwet and Kooyman[18] by the reaction between arenediazonium chloride and sodium arenethiolate at ca. −5 °C, and recrystallized from methanol or ether–methanol. The diazenes prepared are listed in Table 4.

(2) Syntheses of 1,2,3-Benzothiadiazoles. 1,2,3-Benzothiadiazoles were prepared by the method of Jacobson and Janssen[20] by diazotization of 2-mercaptoanilines and purified by distillation (Table 5).

(3) Syntheses of Triazenes. 1-Aryl-3,3-dimethyltriazenes (Ar=4-tolyl, 4-methoxyphenyl) were prepared by the reaction of arenediazonium salts with dimethylamine in aqueous alkaline solution,[21] and purified by sublimation.[22,23] 1-(4-Dimethylaminophenyl)-3,3-dimethyltriazene was obtained by a variant of this method, described by Rondestvedt and Davis.[24] However, the yield was only poor, and the compound decomposed slowly even at room temperature. The triazenes prepared are listed in Table 6.

(4) Isotope-Labelling Experiment. a) Deuterium-Labelling: The deuterium-labelled compounds were prepared by heating the parent anilines to 100 °C in an excess of deuterium oxide (Merck UVASOL, *d*-99.75%)-deuterium chloride for 24 h whereupon the process was repeated 3 times each with a freshly prepared mixture of deuterium oxide–deuterium chloride.

The deuterium exchange was monitored and determined by ^{1}H NMR spectroscopy of aniline deuteriochloride in deuterium oxide.

Diazotization of the deuteriated aniline was also performed in deuterium oxide–deuterium chloride.

For the preparation of 1-(4-*t*-butylphenylthio)-2-(3,5-dideuteriophenyl)diazene, we used 3,5-dideuterioaniline (*d*-98%), obtained from perdeuterioaniline (Merck Co.) by ^{1}H-exchange reaction using H_2O–hydrogen chloride.

b) ^{15}N-Labelling: For the preparation of 1-(4-chlorophenyl)-2-(phenylthio)diazene-2-^{15}N, we diazotizated 4-chloroaniline using sodium nitrite-^{15}N (Prochem Co., ^{15}N-95%).

The ^{15}N-labelled triazenes (Nos. 5—7) were prepared according to the general procedure[21,22] using the respective ^{15}N-labelled starting materials (sodium nitrite-^{15}N, *p*-toluidine-^{15}N, ^{15}N-95%).

(5) ESR Experiment. ESR spectra were taken on a Varian E-109E spectrometer at −104 — −116 °C. About 50 mg of azo sulfide and 2 ml of cyclopropane were sealed in vac. in a Pyrex tube (ϕ 10 mm), carrying a quartz side arm (ϕ 4 mm). The irradiation of the sample was carried out by using a Xe lamp (1 kW) of USHIO Electric Co. Type UXL-1000D-0, Pyrex cylinder lens, a filter glass (420 nm), and a 10 cm water cell filter. Triazenes were irradiated with a Molectron UV-14 and a quartz cylinder lens.

1,2,3-Benzothiadiazoles were illuminated using a Xe lamp and a quartz lens without 420 nm filter in the presence of di-*t*-butyl peroxide, ca. 200 mg.

The *g*-values were determined by reference to the *g*-value of 2.0054[25] of potassium nitrosodisulfonate in a slightly ammoniacal solution.

(6) CINDO Calculations. We employed the standard CNDO and INDO programs[15] on a MELCOM-COSMO 700

Table 4. 1-Aryl-2-(arylthio)diazenes, Ar–N=N–S–C_6H_4–R

No.	Substit. on Ar	R	Mp θ_m/°C	Remarks and Elemental Analysis (%)		
				C	H	N
1	4-$(CH_3)_2N$	4-*t*-C_4H_9	77—78 °C, d	f. 69.23	7.57	13.32
				c. 68.97	7.40	13.41
				for $C_{18}H_{23}N_3S$		
2	4-CH_3O	4-*t*-C_4H_9	50—52 °C, d	lit,[18] mp 50—51 °C		
3	4-CH_3O-2,6-d_2	4-*t*-C_4H_9	48—50 °C, d	*d*-atom% 92%		
4	4-CH_3	4-*t*-C_4H_9	58—61 °C, d	lit,[18] mp 58.5—59.5 °C		
8	3,5-$(CH_3)_2$	4-*t*-C_4H_9	37—38 °C, d	f. 72.38	7.53	9.58
				c. 72.44	7.43	9.39
				for $C_{18}H_{22}N_2S$		
9	H	4-*t*-C_4H_9	34—35 °C, d	lit,[18] mp 33.5—34.5 °C		
10	3,5-d_2	4-*t*-C_4H_9	34—35 °C, d	*d*-atom% 98%		
11	3-CH_3O	4-*t*-C_4H_9	33—34 °C, d	f. 67.81	6.79	9.38
				c. 67.97	6.71	9.32
				for $C_{17}H_{20}N_2OS$		
12	4-Cl	4-H	59—60 °C, d	lit,[18] mp 59.0—59.5 °C		
13	4-Cl-2,6-d_2	4-H	59—60 °C, d	*d*-atom% 94%		
14	4-Cl-2-^{15}N	4-H	59—60 °C, d			
15	4-I	4-*t*-C_4H_9	57—58 °C, d	f. 48.45	4.39	7.30
				c. 48.49	4.32	7.07
				for $C_{16}H_{17}IN_2S$		
16	2-CH_3	4-H	19—20 °C, d	f. 68.27	5.25	12.13
				c. 68.39	5.30	12.27
				for $C_{13}H_{12}N_2S$		
17	2,3-$(CH_3)_2$	4-H	37—38 °C	f. 69.36	5.92	11.58
				c. 69.39	5.82	11.56
				for $C_{14}H_{14}N_2S$		
18	2,5-$(CH_3)_2$	4-H	39—40 °C, d	f. 69.49	5.82	11.57
				c. 69.39	5.82	11.56
				for $C_{14}H_{14}N_2S$		

Table 4. (Continued)

No.	Substit. on Ar	R	Mp θ_m/°C	Remarks and Elemental Analysis (%)		
				C	H	N
19	2,4,6-$(CH_3)_3$	4-H	28—29°C, d	f. 70.37	6.46	10.46
				c. 70.28	6.29	10.93
				for $C_{15}H_{16}N_2S$		
20	2-CH_3S	4-*t*-C_4H_9	61—62°C, d	f. 64.59	6.63	8.42
				c. 64.52	6.37	8.85
				for $C_{17}H_{20}N_2S_2$		
21	2-CH_3O	4-H	59—60°C, d	f. 64.19	4.90	11.41
				c. 63.91	4.95	11.47
				for $C_{13}H_{12}N_2OS$		
22	2-CH_3O-4,6-d_2	4-*t*-C_4H_6	78—80°C, d	f. 67.49		9.14
				c. 67.52		9.26
				for $C_{17}H_{18}D_2N_2OS$		
				NMR of $D_3N^+C_6H_2D_2OCH_3$ (D_2O) 7.03 (s, 1H), 6.91 (s, 1H)		
23	2-CH_3O-5-CH_3	4-H	23.5—24.5°C, d	f. 65.01	5.43	11.05
				c. 65.09	5.46	10.84
				for $C_{14}H_{14}N_2OS$		
24	2-CH_3O-3,5-$(CH_3)_2$	4-*t*-C_4H_9	28—29°C, d	f. 69.59	7.66	8.82
				c. 69.48	7.36	8.53
				for $C_{19}H_{24}N_2OS$		
25	2-F-4,6-d_2	4-*t*-C_4H_9	44—45°C, d	NMR of $D_2HC_6H_2D_2F$ (D_3Cl) 6.97 (d, J_{H-F}: 10 Hz, 1H), 6.91 (s, 1H)		
26	2-Cl	4-H	46—47°C, d	f. 57.78	3.56	11.41
				c. 57.95	3.65	11.26
				for $C_{12}H_9ClN_2S$		
27	2-Cl-4,6-d_2	4-H	45.5—47°C, d	f. 57.53		11.33
				c. 57.48		11.17
				for $C_{12}H_7ClD_2N_2S$		
				NMR of $D_3N^+C_6H_2D_2Cl$ two singlets of arom-H		
28	2-Cl-5-CH_3	4-H	30—32°C, d	f. 59.34	4.18	10.64
				c. 59.43	4.22	10.66
				for $C_{13}H_{11}ClN_2S$		
29	2-Br	4-H	44—45°C, d	f. 49.03	3.01	9.60
				c. 49.16	3.09	9.56
				for $C_{12}H_9BrN_2S$		

Table 5. Benzothiadiazoles

No.	Substit. on Benzene Ring	Mp θ_m/°C	Remarks			
30	(H)	34—36°C	lit,[20] mp 35.5—36°C			
31	4,6-d_2	34—35°C	*d*-atom%: 4-*d* 97%, 6-*d* 99%			
32	5-CH_3	29—30.5°C	C%	H%	N%	S%
			f. 56.30	3.93	18.84	20.96
			c. 55.98	4.03	18.65	21.35
			for $C_7H_6N_2S$			

Table 6. 1-Aryl-3,3-dimethyltriazenes
$Ar\text{-}N^1{=}N^2\text{-}N(CH_3)_2$

No.	Substit. on Ar	Mp θ_m/°C	Remarks
—	4-CH_3	49—50°C	lit,[21] mp 46.5—47.5°C
—	4-CH_3O	oil	lit,[21] bp 59°C/0.75 Torr[a]
—	4-$(CH_3)_2N$	89—91°C	lit,[24] mp 92—93.5°C
5	4-CH_3-2-^{15}N	49—50°C	—
6	4-CH_3-1-^{15}N	49—50°C	—
7	4-CH_3-1,2-$^{15}N_2$	49—50°C	—

a) 1 Torr = 133.322 Pa.

computer (MITSUBISHI Electric Co.).

References

1) Preliminary results of this study were reported in *Chem. Lett.*, **1980**, 1339. The *g*-values were recalculated by reference to the standard value of nitrosodisulfonate (Ref. 24). The assignment of the hydrogen hfs of (2-*t*-butoxythiophenyl)diazenyl radical should be corrected as $a_{3\text{-H}}$=1.32 G instead of $a_{5\text{-H}}$ (Ref. Nos. 30—32 of Table 1).

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