6638 *J. Org. Chem.* 1991, *56*, 6638–6643

Exceptionally Persistent Nitrogen-Centered Free Radicals. Preparation, Isolation, and Molecular Structure of *N*-(Arylthio)-2,4,6-triphenylanilino Radicals[1]

Yozo Miura,*[2] Akio Tanaka,[2] and Ken Hirotsu[3]

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan, and Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received May 16, 1991

The preparation, isolation, molecular structure, and ESR spectra of *N*-(arylthio)-2,4,6-triphenylanilino radicals **2** are described. Radicals **2** have been prepared by oxidation of *N*-(arylthio)-2,4,6-triphenylaniline (**1**) with PbO_2 and studied by ESR spectroscopy. The radical solutions (benzene) were greenish blue or yellowish green, absorbing in the visible region at 513–535 and 626–644 nm. The radicals persist over a long period with only a slight or no decomposition, even in the presence of atmospheric oxygen, and have shown no tendency to dimerize, even at low temperatures. These properties have permitted us to isolate **2** as pure radical crystals and to determine the molecular structure of **2e** by single-crystal X-ray analysis. The ESR spectrum of **2** consists of a broad 1:1:1 triplet (a_N, 0.890–0.896 mT), and hyperfine splittings due to protons were completely unresolved. However, on deuteriation of the 2,4,6-triphenyl groups on the anilino group, hyperfine splittings due to the anilino meta (0.133–0.134) and the arylthiyl ortho protons (0.088 mT) were found. Furthermore, at high gain satellite lines due to ^{33}S isotopes (0.51 mT) at natural abundance were detected. On the basis of these ESR results the spin density distribution in **2** is elucidated.

Introduction

Free radicals are inherently transient because they contain an unpaired electron in the highest occupied molecular obital. However, electronic stabilization and steric protection can drastically change their stabilities. Typical examples are provided by 2,2-diphenyl-1-picrylhydrazyl, 2,4,6-tri-*tert*-butylphenoxy, nitroxides, and 1,3,5-triarylverdazyls, which have been isolated as pure radical crystals.[4] However, in spite of much effort to obtain such exceptionally persistent free radicals, they remain very rare.

As part of a program directed toward the synthesis of high-spin or ferromagnetic materials, we have searched for such exceptionally persistent free radicals since the recent advances in the syntheses of ferromagnetic materials have seriously been limited by the unavailability of free radicals having suitable structures and sufficient stabilities for the construction of ferromagnetic materials.[5] In the course of ESR studies on thioaminyl radicals ($R\dot{N}SR'$), we found that *N*-(arylthio)-2,4,6-triphenylanilino radicals **2** are exceptionally persistent, even in the presence of oxygen, and can be isolated as pure radical crystals.[6] In the present paper we report preparation, isolation, molecular structure, and ESR spectra of **2**.

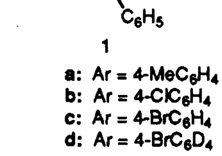
Results and Discussion

Preparation and Isolation of 2. Precursors *N*-(arylthio)-2,4,6-triphenylanilines **1** were prepared by the reaction of 2,4,6-triphenylaniline with arenesulfenyl chlorides in dry ether in the presence of triethylamine. The yields of **1** depended significantly on the substituents on the arenesulfenyl chlorides. Electron-withdrawing substituents such as 2,4-dichloro, 3,5-dichloro-, 3-nitro, or 4-nitro gave **1** in good yields (39–55%), but when arenesulfenyl chlorides having an electron-donating substituent such as 4-methyl were employed, the yields were low (e.g., for **1a**: 11%). It is likely that the presence of an electron-donating substituent leads to destabilization of the N–S bond, and this results in a reduction in the yields of **1**. Our failure in the preparation of *N*-(phenylthio)-2,4,6-triphenylaniline can be in part ascribed to this reason. Futhermore, it was found that when arenesulfenyl chlorides having a bulky group at an ortho position such as 2-nitro- or 2,4-dinitrobenzenesulfenyl chloride were employed, the reaction gave no formation of **1**. This is probably due to steric inhibition of the reaction.

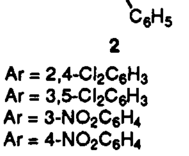
Table I. ESR Parameters for 2 and 4 in Benzene at 21 °C[a]

radical	a_N	a_{other}	g
2a	0.890		2.0058
2b	0.895		2.0057
2c	0.894		2.0059
2d	0.890		2.0059
2e	0.895		2.0055
2f	0.891		2.0054
2g	0.896		2.0055
2h	0.890		2.0054
4a[b]	0.894	0.133 (2 H),[c] 0.088 (2 H)[d]	2.0059
4b[b]	0.894	0.134 (2 H),[c] 0.51 (^{33}S), 1.02 (1 ^{13}C)	2.0059

[a] The hyperfine splitting constants are given in mT. [b] The hyperfine splitting constants are determined by computer simulation. [c] Due to the anilino meta protons. [d] Due to the phenylthiyl ortho protons.



1



2

a: Ar = 4-MeC_6H_4
b: Ar = 4-ClC_6H_4
c: Ar = 4-BrC_6H_4
d: Ar = 4-BrC_6D_4
e: Ar = 2,4-$Cl_2C_6H_3$
f: Ar = 3,5-$Cl_2C_6H_3$
g: Ar = 3-$NO_2C_6H_4$
h: Ar = 4-$NO_2C_6H_4$

Generation of **2** was performed by oxidation of **1** with PbO_2. When PbO_2 was added to a stirred mixture of **1** and K_2CO_3 in benzene, the mixture immediately turned bluish green (**2a–g**) or yellowish green (**2h**) and gave an intense

---

(1) ESR Studies of Nitrogen-Centered Free Radicals. 40. Part 39: Miura, Y.; Tanaka, A. *J. Org. Chem.* 1991, *56*, 3950.

(2) Department of Applied Chemistry, Faculty of Engineering, Osaka City University.

(3) Department of Chemistry, Faculty of Engineering, Osaka City University.

(4) Forrester, A. R.; Hay, J. M.; Thomson, H. R. In *Organic Chemistry of Stable Free Radicals*; Academic Press: London and New York, 1968. Rozantsev, E. G. In *Free Nitroxide Radicals*; Plenum Press: New York and London, 1970. Neugebauer, F. A. *Angew Chem., Int. Ed. Engl.* 1973, *12*, 455.

(5) Mataga, N. *Theoret. Chim. Acta* 1968, *10*, 372. Ovchinnikov, A. A. *Theoret. Chim. Acta* 1978, *47*, 297. Itoh, K. *Pure Appl. Chem.* 1978, *50*, 1251. Iwamura, H. *Pure Appl. Chem.* 1986, *58*, 187. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* 1988, *88*, 201.

(6) Part of this work was reported as a preliminary communication: Miura, Y.; Tanaka, A. *J. Chem. Soc., Chem. Commun.* 1990, 441.

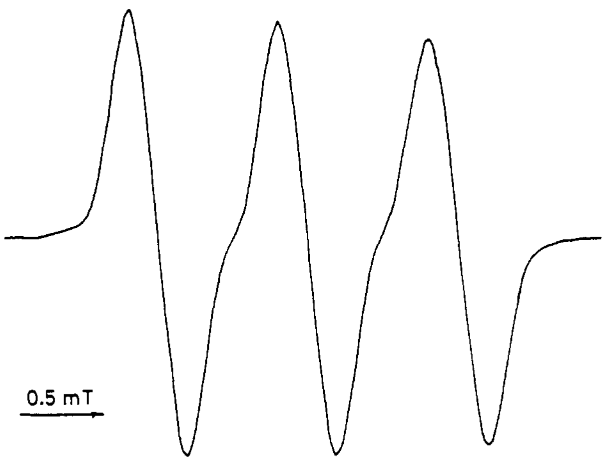


Figure 1. ESR spectrum of **2e** in benzene at 21 °C.

Table II. Selected Bond Lengths and Angles and Dihedral Angles for 2e

Bond Lengths (Å)		Bond Angles (deg)	
C1–C2	1.438 (8)	C2–C1–N	113.3 (5)
C1–C6	1.430 (9)	C6–C1–N	128.2 (5)
C1–N	1.356 (8)	C1–N–S	123.1 (4)
N–S	1.637 (5)	N–S–C25	100.1 (3)
C25–S	1.771 (7)		
Dihedral Angles (deg)			
C2–C1–N–S	−170.5 (4)	N–S–C25–C26	2.2 (6)
C6–C1–N–S	14.6 (9)	N–S–C25–C30	179.8 (5)
C1–N–S–C25	−174.7 (5)		

1:1:1 triplet ESR spectrum. A typical ESR spectrum of **2** is illustrated in Figure 1 and the ESR parameters are summarized in Table I.

Radicals **2** are quite persistent in benzene, even in the presence of atmospheric oxygen. This was shown by a brief kinetic ESR experiment. Although a benzene solution of **2** was placed in an ESR cell, and ESR spectra from the solution in the unsealed ESR cell were measured at room temperature (22 °C) over 5 h, no or negligibly small reduction in the ESR signal intensity was found during the period. Furthermore, radicals **2** showed no tendency to dimerize, even at low temperatures. This was shown by the observation that the doubly integrated ESR spectrum was linearly increased with $1/T$ (T: 223–303 K). This exhibits that **2** exists solely as individual radicals in solution. These interesting findings prompted us to isolate them, and **2b**, **2c**, and **2e–h** were isolated in 15–63% yields as pure dark green or purple brown crystals by the procedures described in the Experimental Section. In the case of **2a**, however, no pure radical crystals could be obtained. The radicals isolated were quite stable and could be stored at 0 °C for months without decomposition.

Single-Crystal X-ray Analysis. X-ray crystallographic analysis of **2e** was performed to unambiguously establish the structure of **2**. Crystals suitable for the X-ray analysis were grown from hexane. Figure 2 shows the ORTEP drawing of the molecular structure.[7] Selected bond lengths and angles and dihedral angles are listed in Table II. The interplanar angle between the benzene rings A and C is 27.3°. On the other hand, those between the A and B rings and between the A and D rings are 49.2 and 86.7°, respectively. The large angles between the A and B rings and the A and D rings reflect the steric congestion around the N–S bond surrounded by two benzene rings B and D [C8---N = 2.920 (7), C20---S = 3.373 (7), and C24---S = 3.100 (7) Å]. The S and N atoms are coplanar with the benzene ring E within 0.03 Å. This planar group makes an angle of 18.7° with the benzene ring A. On the basis of the nearly planar conformation of the ring A–N–S–ring E moiety, the unpaired electron is expected to be delocalized over the whole of the radical (except the B, C, and D benzene rings). Indeed, this is shown by the observation of the relatively large hyperfine splittings due to the anilino meta (0.133–0.134) and arylthioyl ortho protons (0.088 mT), as described below.

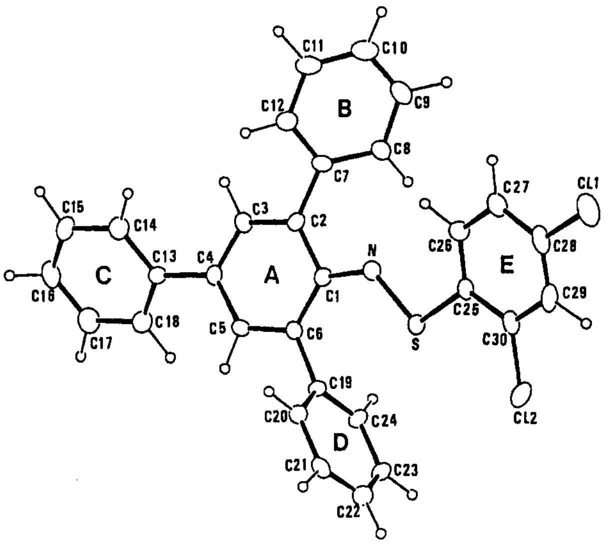


Figure 2. ORTEP drawing of **2e**.

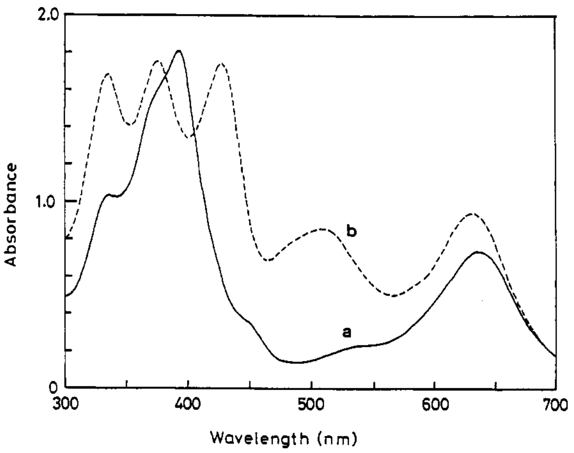


Figure 3. UV–vis spectra of **2e** and **2h** in benzene: (a) **2e**, 8.29×10^{-5} M; (b) **2h**, 1.078×10^{-4} M.

Stabilities of 2. The kinetic studies on all **2** by the ESR or visible spectroscopic method showed that, at room temperature, radicals **2** persist not only in hydrocarbon solvents such as benzene, toluene, and hexane but also in polar solvents such as acetone, ethyl acetate, acetonitrile, dichloromethane, and ethanol, with no or negligibly small decomposition, even in the presence of oxygen. In THF, however, the radicals were slowly decomposed, and in solvents containing organic or inorganic acids immediate decomposition of **2** was found. For example, addition of one drop of concd HCl to a solution of **2** in acetone led to a spontaneous decomposition of **2**. From the solution 2,4,6-triphenylaniline was isolated in quantitative yield (98%) after column chromatographic separation. We therefore carefully removed acids from the solvents used and precursors **1**. For example, the solvents used in crystallization or kinetic studies were of UV grade, and acidic contaminants that might exist in **1** were removed

---

(7) Johnson, C. K. ORTEP, Oak Ridge National Laboratory Report, ORNL-TM-3794, 1965.

Table III. UV-Vis Spectral Data for 2 in Benzene

radical	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})
2a	644, 533, 384
2b	637 (8520), 535 (2460), 391 (20 600), 337 (12 200)
2c	637 (8540), 535 (2440), 391 (20 400), 337 (12 000)
2e	637 (8980), 535 (2790), 394 (22 000), 336 (12 600)
2f	628 (8740), 535 (2780), 392 (23 800), 337 (13 300)
2g	626 (7820), 523 (2890), 381 (21 100), 338 (15 200)
2h	637 (9100), 513 (8300), 430 (16 800), 377 (17 000), 337 (16 300)

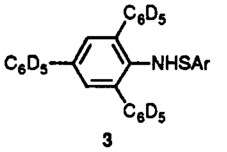
by passing it through an alumina column.

UV-Vis Spectra. Radicals 2 are characterized by the bluish green (**2a-g**) or yellowish green color (**2h**). Typical UV-vis spectra are illustrated in Figure 3, and the UV-vis absorption data are summarized in Table III.

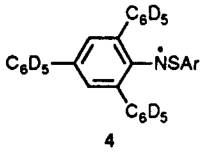
As found in Figure 3, **2e** absorbs in the UV region at 336 and 394 nm and in the visible region at 637 and 535 nm (shoulder). Owing to the combination of the strong absorption at 637 nm (ϵ: 8980) and the weak absorption at 535 nm (ϵ: 2790 L mol^{-1} cm^{-1}) the radical shows a bluish green color. Very similar UV-vis spectra were obtained from the solutions of **2a-c**, **2f**, and **2g**. On the other hand, radical **2h** gave a considerably different UV-vis spectrum owing to the presence of the *p*-nitro group (see: Figure 3). Since radicals 2 have an intense absorption (ϵ: 7820-9100 L mol^{-1} cm^{-1}) in the visible region, we can easily determine radical concentrations from the visible spectra. In the kinetic decay studies on 2, the radical concentrations were also followed by measuring the visible spectra.

ESR Spectra. Radicals 2 gave a broad 1:1:1 triplet ESR spectrum with large peak-to-peak line widths of ~0.33 mT, and proton hyperfine splittings were unresolved. This is ascribable to the presence of numerous unresolved aromatic protons. For the elucidation of the spin density distribution in 2, however, the evaluation of the proton hyperfine splitting constants is necessary. We therefore prepared some partially deuteriated radicals 2.

Radical **2d** whose phenylthiyl group is fully deuteriated, however, still gave a 1:1:1 triplet ESR spectrum, although the peak-to-peak line width was reduced from 0.33 to 0.30 mT. This indicates that the line broadening in the ESR spectra of 2 can be ascribable to the many unresolved protons of the three substituted phenyl groups, and this result forced us to prepare 2,4,6-triphenyl-deuteriated radicals such as **4a** and **4b**. Precursor **3** was prepared by the reaction of 2,4,6-triphenyl-d_{15}-aniline with the corresponding arenesulfenyl chlorides, and the deuteriated aniline was prepared from acetophenone-d_5 and benzaldehyde-d_5 according to the literature procedures for the corresponding nonlabeled compound. The oxidation of **3** was performed with PbO_2, analogously to the case of 2.



3



4

a: Ar = 4-BrC_6H_4
b: Ar = 4-BrC_6D_4

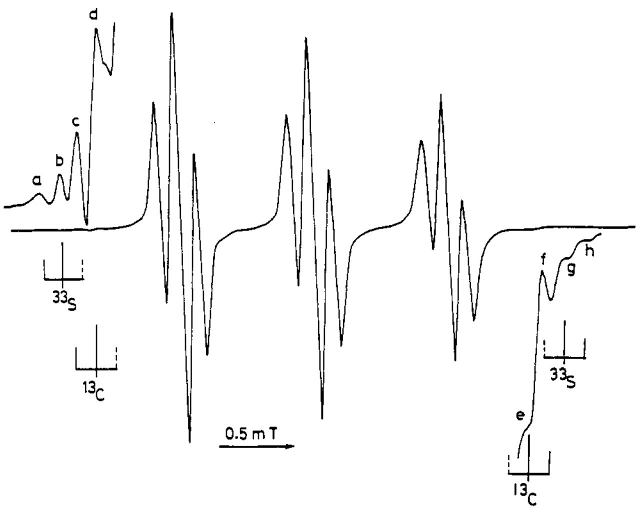


Figure 4. ESR spectrum of **4b** in benzene at 21 °C. Both wings are recorded at high gain (100 times), and satellite lines due to ^{33}S isotopes (a and b, $M_N = +1$, $M_S = +^3/_2$; *g* and *h*, $M_N = -1$, $M_S = -^3/_2$) and satellite lines due to ^{13}C isotopes (c and d, $M_N = +1$, $M_C = +^1/_2$; e and f, $M_N = -1$, $M_C = -^1/_2$) are found.

Table IV. Comparison of ESR Parameters for 4 with Those for 5, 6, and 7[a]

radical	a_N	$a_{o\text{-H}}$[b]	$a_{m\text{-H}}$[b]	$a_{p\text{-H}}$[b]	$a_{o\text{-H}}$[c]	$a_{^{33}S}$	g
4a	0.894		0.133		0.088		2.0059
4b	0.894		0.134			0.51	2.0059
5	0.959	0.370	0.126	0.418	0.078		2.0059
6 (Ar = C_6D_5)	0.952	0.373		0.423		0.462	2.0060
7	1.230						2.0066

[a] The hyperfine splitting constants are given in mT. [b] The protons on the anilino benzene ring. [c] The protons of the arylthiyl group.

Figure 4 shows an ESR spectrum of **4b** in benzene. Hyperfine splittings due to the anilino meta protons are found. In the ESR spectrum of **4a** hyperfine splittings due to the anilino meta and arylthiyl ortho protons were also observed. Furthermore, in the spectrum of **4b** satellite lines due to ^{33}S at natural abundance, together with satellite lines due to ^{13}C at natural abundance, were detected in the wings where the spectrum was recorded at high gain. The assignments of these satellite lines were performed on the basis of the intensities (heights) of the satellite lines appearing in the left wing of the parent spectrum. The natural abundances of ^{33}S ($I = ^3/_2$) and ^{13}C isotopes ($I = ^1/_2$) are 0.76 and 1.11%, respectively. Thus, the intensity ratios of the satellite lines due to ^{33}S and ^{13}C at natural abundance to the parent spectrum are 0.19 and 0.55%, respectively. In the case of ^{13}C the observed value for lines c and d in Figure 4 is 0.46%, being in good agreement with the theoretical one. In the case of ^{33}S the observed value for lines a and b (0.073%) is significantly lower than the theoretical one. However, the $a_{^{33}S}$ value obtained (0.51 mT) lies in the range of those (0.39-0.593 mT) reported for the structurally related thioaminyl radicals examined.[8,9] We therefore determined that the satellite lines are due to ^{33}S isotopes. The large difference between the observed and theoretical intensities is probably caused by the increased line width of the ^{33}S satellite lines as compared to the parent spectrum. Additional reason might be the overlap of the ^{33}S satellite lines and the more intense ^{13}C satellite lines. By this overlap the intensities of the satellite lines due to ^{33}S isotope might be reduced. The ^{14}N, ^{1}H, ^{33}S, and ^{13}C hyperfine splitting constants for **4a** and **4b** are listed in Table I.

As found in Table IV the a_N and $a_{^{33}S}$ values for 2 and 4 are very similar to those for their analogues, **5** and **6**, indicating that the spin distribution patterns in 2 and 4 are essentially the same as those in these analogues. That is, in 2 the unpaired electron is delocalized over the whole

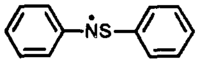
---

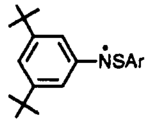
(8) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M. *J. Org. Chem.* **1980**, *45*, 3875.

(9) Miura, Y.; Asada, H.; Kinoshita, M.; Ohta, K. *J. Phys. Chem.* **1983**, *87*, 3450.

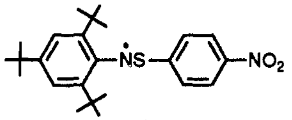
(10) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142.

of the radicals (except the 2,4,6-triphenyl groups), and high spin density positions are the nitrogen, sulfur, and anilino ortho and para carbons. On the basis of these ESR results, the high *g* values for **2** and **4** are ascribable to the high spin density on sulfur having a large spin–orbit coupling parameter (382 cm^{-1}), which shifts the *g* values to higher ones.


5



6



7

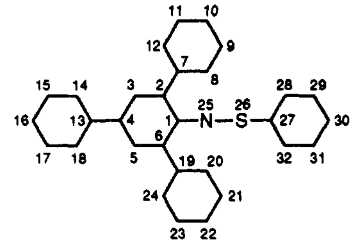
For the spin density distribution in **2** to be elucidated in more detail, the Hückel and McLachlan–Hückel MO calculations were performed by using the following parameters: $\alpha_N = \alpha + 0.6\beta$, $\alpha_S = \alpha + \beta$, $\beta_{CN} = 1.1\beta$, $\beta_{NS} = 0.7\beta$, $\beta_{CS} = 0.7\beta$, $\lambda = 0.7$. These parameters have always been employed in our calculations on thioaminyl radicals.[9] The Coulomb integrals between C2–C7, C4–C13, C6–C19, and C1–N are estimated, on the basis of the X-ray results of **2e**, as follows: $\beta_{C2-C7} = (\cos^2 49.2°)\ \beta = 0.43\beta$, $\beta_{C4-C13} = (\cos^2 27.3°)\ \beta = 0.79\beta$, $\beta_{C6-C19} = (\cos^2 86.7°)\ \beta = 0$, $\beta_{C1-N} = (\cos^2 18.7°)\ \beta_{CN} = 0.90\beta_{CN}$. As found in Table V, the calculations are in good agreement with the experiments and predict that the unpaired electron resides mainly on N, S, C2, C4, and C6. The calculations also predict that there is only a small delocalization of the unpaired electron onto the benzene ring labeled C and that there is no or negligibly small delocalization of the unpaired electron into the benzene rings labeled B and D in Figure 2. On the basis of the experimental and theoretical results, it is obvious that the three benzene rings do not play an important role in delocalizing the unpaired electron. It can therefore be concluded that these substituents contribute to the stability of **2** as protecting groups.

Although the substituted three phenyl groups do not play an important role in delocalizing the unpaired electron, their presence changes slightly the spin densities on nitrogen and sulfur by their inductive effects. As found in Table IV, the a_N values for **2** and **4** are somewhat smaller than those for **5** and **6**, while the $a_{^{33}S}$ value is somewhat larger than that for **6**. Like **5**, **6**, and **7**, **2** and **4** can be represented by two canonical forms **8** and **9**. If canonical form **9** is enhanced, the a_N values will be reduced, while the $a_{^{33}S}$ values will be increased. The presence of the substituted triphenyl groups is just the case. Furthermore, additional reduction in a_N may take place owing to the samll delocalization of the unpaired electron onto the C benzene ring.


$$-\dot{N}-\ddot{S}- \longleftrightarrow -\ddot{N}^{-}-\dot{S}^{+}-$$

8 **9**

Table V. Experimental and Calculated Spin Density Distribution in 2



position	obsd hfs const[a]	exptl spin density[b]	calcd spin density	
			HMO	McLachlan[c]
1			0.001	–0.040
2			0.081	0.096
3	0.133[d]	0.049	0.000	–0.025
4			0.082	0.086
5	0.133[d]	0.049	0.000	–0.026
6			0.081	0.099
7			0.000	–0.002
8, 12			0.004	0.004
9, 11			0.000	–0.001
10			0.004	0.004
13			0.000	–0.006
14, 18			0.013	0.013
15, 17			0.000	–0.004
16			0.013	0.012
19			0.000	0.000
20, 24			0.000	0.000
21, 23			0.000	0.000
22			0.000	0.000
25 (N)	0.894[d]	0.41	0.400	0.518
26 (S)	0.51[e]	0.22	0.223	0.215
27			0.000	–0.013
28, 32	0.088	0.033	0.027	0.026
29, 31			0.000	–0.008
30			0.027	0.024

[a] The hyperfine splitting (hfs) constants are given in mT. [b] Calculated from the equation, $a_x = Q_x\sigma_x^{\pi}$, where $Q_H = -2.7$, $Q_N = 2.2$, $Q_{33} = 2.3$ mT.[9] [c] $\lambda = 0.7$. [d] Hyperfine splitting constants for **4a**. [e] Hyperfine splitting constants for **4b**.

Origin of the Exceptional Stability of 2. It has previously been reported that thioaminyls including **5**, **6**, and **7** are largely stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the adjacent sulfur[9] (**8** ↔ **9**). However, **5** is not so long-lived in solution. It is immediately destroyed by irreversible homolytic reactions occurring at the ortho and para positions of the anilino benzene ring. The detailed decomposition mechanisms were previously reported by us[11] and by Benati et al.[12] Radicals **6**, in which anilino ortho and para positions are sufficiently protected by *tert*-butyl groups, persist over a long period, even in the presence of oxygen. However, this is in equilibrium in solution with the corresponding isolable hydrazine-like dimer having a weak N–N bond energy (56.8 kJ mol^{-1}).[7] On the other hand, radical **7** exists solely as individual radicals in solution owing to the presence of three *tert*-butyl groups which protect both the nitrogen and anilino ortho and para positions.[13] It can therefore be isolated as pure radical crystals. The X-ray results exhibited that the radical adopts a twisted conformation in which the coplane consisting of the nitrogen and the phenylthiyl group makes an angle of 90.7 with the anilino benzene ring due to the steric congestion around the N–S bond surrounded by two ortho *tert*-butyl groups. Owing to this twisted structure **7** loses the electronic stabilization by the anilino benzene ring. For this reason **7** is destroyed in solution by oxygen. In contrast, radicals **2** still keep a planar structure, in spite of the introduction of three phenyl groups into the anilino ortho and para positions, as shown by the X-ray analysis. Thus, radicals **2** are insensitive toward oxygen. In conclusion, the exceptional persistence of **2** can be ascribed to the following three points: (1) radicals **2** are greatly

---

(11) Miura, Y.; Yamamoto, A.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3215.

(12) Balboni, C.; Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2111.

(13) Miura, Y.; Yamamoto, A.; Katsura, Y.; Kinoshita, M.; Sato, S.; Tamura, C. *J. Org. Chem.* **1982**, *47*, 2618.

stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur; (2) the radical center and the anilino group are effectively protected by the three phenyl groups introduced into the anilino benzene ring from the reversible N–N dimerization and from the irreversible reactions that destroy **2**; (3) in spite of the presence of the three phenyl groups, the main framework of radicals **2** still keep a planar structure and hence do not react with oxygen.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run on a JASCO A-202 spectrophotometer and UV–vis spectra on a Shimadzu UV-240 spectrophotometer. ^{1}H NMR were recorded on a JEOL GX-400 spectrometer (400 MHz), and chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane used as internal standard.

4-Methyl-, 4-chloro-, 4-bromo-, 2,4-dichloro-, 3,5-dichloro-, 3-nitro-, and 4-nitrobenzenesulfenyl and 4-bromobenzenesulfenyl-d_4 chlorides were obtained by passing chlorine through a solution of the corresponding arenethiol or diaryl disulfide in dry CH_2Cl_2 or $CHCl_3$ at 0 °C or at room temperature by the usual method.[1] 4-Methylbenzenesulfenyl chloride was purified by distillation, while the other sulfenyl chlorides were used in the following step without further purification.

General Procedure for Preparation of *N*-(Arylthio)-2,4,6-triphenylanilines 1a–h. To a stirred solution of 2.00 g (6.22 mmol) of 2,4,6-triphenylaniline and 1.16 g (11.5 mmol) of triethylamine in 100 mL of dry ether was added a solution of 6.76 mmol of arenesulfenyl chloride in 30 mL of dry ether at 0 °C. After the addition was completed, the dark green reaction mixture was stirred for 2 h at the same temperature, filtered, and evaporated under reduced pressure. The resulting residue (viscous oil or solid) was chromatographed on alumina (Merck, aluminium oxide 90; column size 3.5 × 30 cm) using 1:3 benzene–hexane (**1a–f**), 1:2 benzene–hexane (**1g**), or 1:1 benzene–hexane (**1h**) as eluant, giving **1** as a pure solid or as a solid containing small amounts of 2,4,6-triphenylaniline diaryl disulfide.[14]

***N*-[(4-Methylphenyl)thio]-2,4,6-triphenylaniline (1a)**: colorless needles (from ethanol); mp 138–139 °C; 0.293 g (0.672 mmol, 11%); IR (KBr) 3350 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, Me, 1 H), 5.38 (s, NH, 1 H), 6.75–7.61 (m, aromatic, 21 H). Anal. Calcd for $C_{31}H_{25}NS$: C, 83.93; H, 5.68; N, 3.16. Found: C, 83.99; H, 5.71; N, 3.18.

***N*-[(4-Chlorophenyl)thio]-2,4,6-triphenylaniline (1b)**: colorless needles (from ethanol); mp 119–120 °C; 1.65 g (3.56 mmol, 57%); IR (KBr) 3330 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.41 (s, NH, 1 H), 6.73–7.61 (m, aromatic, 21 H). Anal. Calcd for $C_{30}H_{22}ClNS$: C, 77.65; H, 4.78; N, 3.02. Found: C, 77.42; H, 4.86; N, 3.03.

***N*-[(4-Bromophenyl)thio]-2,4,6-triphenylaniline (1c)**: light green prisms (from ethanol–benzene); mp 142–144 °C; 0.80 g (1.57 mmol, 25%); IR (KBr) 3310 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.41 (s, NH, 1 H), 6.65–7.61 (m, aromatic, 21 H). Anal. Calcd for $C_{30}H_{22}BrNS$: C, 70.86; H, 4.36; N, 2.76. Found: C, 71.13; H, 4.47; N, 2.64.

***N*-[(4-Bromophenyl-d_4)thio]-2,4,6-triphenylaniline (1d)**: light green prisms (from ethanol–benzene); mp 144–145.5 °C; 0.75 g (1.48 mmol, 24%); IR (KBr) 3310 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.40 (s, NH, 1 H), 7.17–7.60 (m, aromatic, 17 H). Anal. Calcd for $C_{30}H_{18}BrD_4NS$: C, 70.31; H, 4.33; N, 2.73. Found: C, 69.94; H, 4.20; N, 2.51.

***N*-[(2,4-Dichlorophenyl)thio]-2,4,6-triphenylaniline (1e)**: colorless needles (from ethanol–benzene); mp 142–143 °C; 1.33 g (2.67 mmol, 43%); IR (KBr) 3210 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.27 (s, NH, 1 H), 6.89–7.60 (m, aromatic, 20 H). Anal. Calcd for $C_{30}H_{21}Cl_2NS$: C, 72.28; H, 4.25; N, 2.81. Found: C, 72.47; H, 4.45; N, 2.92.

***N*-[(3,5-Dichlorophenyl)thio]-2,4,6-triphenylaniline (1f)**: colorless prisms (from ethanol); mp 57–59 °C; 1.68 g (3.37 mmol, 54%); IR (KBr) 3330^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.38 (s, NH, 1 H), 6.63–7.60 (m, aromatic, 20 H). Anal. Calcd for $C_{30}H_{21}Cl_2NS$: C, 72.28; H, 4.25; N, 2.81. Found: C, 71.98; H, 4.29; N, 2.68.

***N*-[(3-Nitrophenyl)thio]-2,4,6-triphenylaniline (1g)**: light yellow needles (from ethanol–benzene); mp 145–146.5 °C; 1.63 g (3.44 mmol, 55%); IR (KBr) 3300 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.42 (s, NH, 1 H), 7.04–7.83 (m, aromatic, 21 H). Anal. Calcd for $C_{30}H_{22}N_2O_2S$: C, 75.92; H, 4.67; N, 5.90. Found: C, 75.96; H, 4.70; N, 5.85.

***N*-[(4-Nitrophenyl)thio]-2,4,6-triphenylaniline (1h)**: light greenish yellow prisms (from ethanol–benzene); mp 149–150 °C; 1.37 g (2.44 mmol, 39%); IR (KBr) 3300 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 5.37 (s, NH, 1 H), 6.86–7.88 (m, aromatic, 21 H). Anal. Calcd for $C_{30}H_{22}N_2O_2S$: C, 75.92; H, 4.67; N, 5.90. Found: C, 76.18; H, 4.73; N, 5.54.

Benzal-*2,3,4,5,6*-d_5-acetophenone-*2,3,4,5,6*-d_5.[15] To a solution of 5.5 g (0.14 mol) of sodium hydroxide in 50 mL of water and 31 mL of 95% ethanol was added 17.5 g (0.140 mol) of acetophenone-*2,3,4,5,6*-d_5. After the mixture was cooled to 0 °C, 15.6 g (0.140 mol) of benzaldehyde-*2,3,4,5,6*-d_5 was added with stirring. The resulting mixture was then stirred at 20–25 °C for 3 h and cooled at 0 °C overnight. The crystalline product was filtered and washed with water and ice-cold 95% ethanol. Recrystallization from 95% ethanol gave 28.2 g (0.129 mol, 92%) of the product: colorless needles; mp 54.5–56 °C; ^{1}H NMR ($CDCl_3$) δ 7.53 (d, J = 15.6 Hz, —CH═, 1 H), 7.82 (d, J = 15.6 Hz, —CH═, 1 H).

2,4,6-Triphenyl-d_{15}-pyrylium Tetrafluoroborate.[16] A solution of 28.2 g (0.129 mol) of benzal-*2,3,4,5,6*-d_5-acetophenone-*2,3,4,5,6*-d_5 and 8.07 g (0.0645 mol) of acetophenone-*2,3,4,5,6*-d_5 in 45 mL of 1,2-dichloroethane was heated at 70–75 °C. To the solution was added 21 mL of a 52% ethereal solution of fluoroboric acid during 0.5 h with stirring. After the addition was completed, the mixture was heated to reflux for 1 h with stirring and cooled at 0 °C overnight. The yellow needles that formed (18.8 g, 0.0433 mol, 67%) were filtered and washed with ether. This product was used in the following step without any purification. A sample with mp 230–235 °C for analysis was obtained by recrystallization from 1,2-dichloroethane.

2,4,6-Triphenyl-d_{15}-nitrobenzene.[17] To a stirred solution of 17.8 (0.0433 mol) of 2,4,6-triphenyl-d_{15}-pyrylium tetrafluoroborate and 3.4 g (0.056 mol) of nitromethane in 50 mL of absolute ethanol was added rapidly 7.3 g (0.072 mol) of triethylamine. The resulting mixture was then heated to reflux for 3 h and cooled at 0 °C overnight. The crystalline product was filtered and washed with small portion of ice-cold methanol. Recrystallization from acetic acid gave 9.26 g (0.0253 mol, 58%) of slightly yellow needles: mp 145–146 °C; ^{1}H NMR ($CDCl_3$) δ 7.62 (s, aromatic, 2 H).

2,4,6-Triphenyl-d_{15}-aniline.[18] Onto 365 g of sodium amalgam, prepared from 350 g of mercury and 15 g of sodium, was added 250 mL of absolute methanol and 9.26 g (0.0253 mol) of 2,4,6-triphenyl-d_{15}-nitrobenzene, and the mixture was then refluxed for 5 h (during which time crystals were not completely dissolved). After cooling, the methanol solution was decanted. The remaining crystals were dissolved in benzene, and the benzene solution was decanted. The combined methanol–benzene solution was washed with water, dried (MgSO4), and evaporated. Upon addition of a small portion (ca. 5 mL) of methanol, the residual oil solidified to slightly yellow microprisms. The crystals were filtered, washed with a small portion of ice-cold methanol, and dried in vacuo: yield 7.33 g (0.0218 mol, 85%); mp 121–123 °C; IR (KBr) 3400 and 3300 (NH_2), 2240 cm^{-1} (C–D); ^{1}H NMR ($CDCl_3$) δ 3.87 (br s, NH_2, 2 H), 7.40 (s, aromatic, 2 H).

***N*-[(4-Bromophenyl)thio]-2,4,6-triphenyl-d_{15}-aniline (3a).** This aniline was prepared by the same procedure as described above. Thus, a solution of 0.73 g (3.37 mmol) of 4-bromobenzenesulfenyl chloride in 15 mL of dry ether was added to a solution of 1.00 g (2.97 mmol) of 2,4,6-triphenyl-d_{15}-aniline and 0.58 g (5.8 mmol) of triethylaniline in 50 mL of dry ether with

---

[14] During column chromatography, part of **1** may be decomposed to give 2,4,6-triphenylaniline and diaryl disulfide. These compounds were removed by the following crystallization.

[15] Kohler, E. P.; Chadwell, H. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. 1, p 78.

[16] Dimroth, K.; Reichardt, C.; Vogel, K. *Org. Synth.* **1969**, *49*, 121.

[17] Dimroth, K.; Berndt, A.; Reichardt, C. *Org. Synth.* **1969**, *49*, 114.

[18] Dimroth, K.; Berndt, A.; E.; H.; Reichardt, C. *Org. Synth.* **1969**, *49*, 116.

stirring at 0 °C. After the addition was completed, stirring was continued for 2 h at the same temperature. The reaction mixture was filtered, evaporated, and the resulting residue was chromatographed using 1:4 benzene–hexane as eluant. Crystallization from ethanol–benzene gave light green prisms; mp 144–146 °C. Yield 0.35 g (0.67 mmol, 22%); IR (KBr) 3330 (NH), 2250 cm^{-1} (C–D); ^{1}H NMR (CDCl$_3$) δ 5.41 (s, NH, 1 H), 6.66 (d, J = 8.5 Hz, aromatic, 2 H), 7.16 (d, J = 8.5 Hz, aromatic, 2 H), 7.42 (s, aromatic, 2 H). Anal. Calcd for $C_{30}H_7BrD_{15}NS$: C, 68.83; H, 4.24; N, 2.68. Found: C, 69.00; H, 4.31; N, 2.59.

***N*-[(4-Bromophenyl-d_4)thio]-2,4,6-triphenyl-d_{15}-aniline (3b).** This aniline was prepared by the same procedure as described above from 1.00 g (2.97 mmol) of 2,4,6-triphenyl-d_{15}-aniline and 0.74 g (3.3 mmol) of 4-bromobenzenesulfenyl-d_4 chloride. Chromatography (eluant 1:4 benzene–hexane) and crystallization (ethanol–benzene) gave 0.30 g (0.57 mmol, 19%) of **3b** as light green prisms: mp 143–145 °C; IR (KBr) 3300 (NH), 2250 cm^{-1} (C–D); ^{1}H NMR (CDCl$_3$) δ 5.41 (s, NH, 1 H), 7.42 (s, aromatic, 2 H). Anal. Calcd for $C_{30}H_3BrD_{19}NS$: C, 68.30; H, 4.20; N, 2.66. Found: C, 68.51; H, 4.35; N, 2.55.

Isolation of *N*-(Arylthio)-2,4,6-triphenylanilino Radicals 2. A mixture of 200 mg of 1 and 1.0 g of K_2CO_3 in 20 mL of benzene was stirred for 1 min. To the vigorously stirred mixture was added 0.8–1.0 g of PbO_2 in some portions during 2 min, and stirring was continuing for an additional 1 min. After filtration, the solvent was removed by freeze-drying and the resulting dark green crystalline residue was crystallized from the appropriate solvents.

***N*-[(4-Chlorophenyl)thio]-2,4,6-triphenylanilino radical (2b)**: dark green needles (from hexane); mp 115–117 °C; 35 mg (0.076 mmol, 18%); IR (KBr) 3070–3000, 1590, 1570, 1490, 1470, 1440, 1385, 1090, 1030, 1010, 890, 810, 760, 700, 605, 580, 480 cm^{-1}. Anal. Calcd for $C_{30}H_{21}ClNS$: C, 77.82; H, 4.57; N, 3.03. Found: C, 78.03; H, 4.69; N, 2.95.

***N*-[(4-Bromophenyl)thio]-2,4,6-triphenylanilino radical (2c)**: dark greenish blue microneedles (from hexane); mp 127–128 °C; 75 mg (0.148 mmol, 38%); IR (KBr) 3070–3000, 1570, 1490, 1460, 1220, 1060, 1000, 890, 820, 810, 760, 750, 700, 580, 480 cm^{-1}. Anal. Calcd for $C_{30}H_{21}BrNS$: C, 71.00; H, 4.17; N, 2.76. Found: C, 71.23; H, 4.25; N, 2.54.

***N*-[(2,4-Dichlorophenyl)thio]-2,4,6-triphenylanilino radical (2e)**: dark purplish brown needles (from hexane); mp 122–123.5 °C; 103 mg (0.207 mmol, 52%); IR (KBr) 3070–3000, 1560, 1540, 1480, 1440, 1370, 1220, 1090, 1070, 1030, 880, 860, 820, 800, 770, 760, 750, 710, 700 cm^{-1}. Anal. Calcd for $C_{30}H_{20}Cl_2NS$: C, 72.43; H, 4.05; N, 2.82. Found: C, 72.25; H, 4.03; N, 2.57.

***N*-[(3,5-Dichlorophenyl)thio]-2,4,6-triphenylanilino radical (2f)**: dark green microneedles (from hexane); mp 140–141 °C; 103 mg (0.207 mmol, 52%); IR (KBr) 3070–3000, 1560, 1490, 1440, 1410, 1400, 1220, 1140, 1100, 1070, 1030, 890, 850, 840, 820, 800, 760, 710, 700, 660, 580 cm^{-1}. Anal. Calcd for $C_{32}H_{20}Cl_2NS$: C, 72.43; H, 4.05; N, 2.82. Found: C, 72.44; H, 4.09; N, 2.72.

***N*-[(3-Nitrophenyl)thio]-2,4,6-triphenylanilino radical (2g)**: dark blue needles (from hexane–ethyl acetate); mp 140–142 °C; 87 mg (0.184 mmol, 44%); IR (KBr) 3050–3000, 1590, 1560, 1520, 1480, 1440, 1340, 1270, 1220, 1180, 1155, 1120, 1070, 1020, 920, 890, 875, 820, 800, 770, 760, 745, 730, 700, 660, 580 cm^{-1}. Anal. Calcd for $C_{30}H_{21}N_2O_2S$: C, 76.08; H, 4.47; N, 5.92. Found: C, 76.12; H, 4.34; N, 5.90.

***N*-[(4-Nitrophenyl)thio]-2,4,6-triphenylanilino radical (2h)**: dark purplish brown needles (from hexane–ethyl acetate); mp 146–147 °C; 125 mg (0.264 mmol, 63%); IR (KBr) 3050–3000, 1570, 1510, 1330, 1220, 1070, 890, 840, 820, 760, 740, 700 cm^{-1}. Anal. Calcd for $C_{30}H_{21}N_2O_2S$: C, 76.08; H, 4.47; N, 5.92. Found: C, 76.04; H, 4.44; N, 5.67.

Decomposition of 2 with HCl. To a stirred solution of 95 mg (0.191 mmol) of **2e** in 20 mL of acetone was added one drop of concd HCl. The green color immediately disappeared and a colorless solution was given. After the acetone solution was diluted with 30 mL of benzene, the solution was washed with 5% $CaCO_3$ (30 mL) and brine (30 mL). After concentration, the residue was column chromatographed on alumina using 1:3 benzene–hexane to give 60.1 mg (0.187 mmol, 98%) of 2,4,6-triphenylaniline; mp 122–124 °C (from methanol).

ESR Measurements. ESR spectra were measured on a JEOL JES-ME-3X or Bruker EP300 spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and g values were determined by the simultaneous measurement with a dilute Fremy's salt in dilute K_2CO_3 aqueous solution (a_N = 1.309 mT; g = 2.0057) as reference. Estimated accuracy: ±0.01 mT for a_N, a_H, $a_{^{33}S}$, and $a_{^{13}C}$ and ±0.0002 for g.

Crystal Data. $C_{30}H_{20}Cl_2NS$, M = 497.47, monoclinic, space group $P2_1/a$, a = 25.765 (9), b = 6.317 (3), and c = 15.533 (5) Å, β = 104.42 (4)°, U = 2448 (2) Å^3, Z = 4, D_c = 1.35 g cm^{-3}, μ = 3.65 cm^{-1}. A total of 3356 reflections with $2\theta < 50°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo Kα radiation. Of these 1991 [with $F > 3\sigma(F)$] were judged to be observed. The structure was solved using MULTAN.[19] All hydrogen atoms could be located on a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to R = 0.062 and R_w = 0.064.[20] Atomic coordinates and parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center.

Registry No. **1a**, 136489-93-5; **1b**, 128529-38-4; **1c**, 128529-39-5; **1d**, 136490-36-3; **1e**, 128529-40-8; **1f**, 128529-41-9; **1g**, 136489-94-6; **1h**, 136489-95-7; **2b**, 128529-42-0; **2c**, 128529-43-1; **2e**, 128529-44-2; **2f**, 128529-45-3; **2g**, 136490-02-3; **2h**, 136490-03-4; **3a**, 136490-00-1; **3b**, 136490-01-2; *p*-ClC_6H_4SCl, 933-01-7; *p*-BrC_6H_4SCl, 1762-76-1; *p*-BrC_6D_4SCl, 133886-90-5; *m*-$NO_2C_6H_4SCl$, 37692-14-1; *p*-$NO_2C_6H_4SCl$, 937-32-6; PbO_2, 1309-60-0; *p*-$CH_3C_6H_4SCl$, 933-00-6; 2,4,6-triphenylaniline, 6864-20-6; 2,4-dichlorobenzenesulfenyl chloride, 38064-02-7; 3,5-dichlorobenzenesulfenyl chloride, 74282-78-3; benzal-*2,3,4,5,6-d*$_5$-acetophenone-*2,3,4,5,6-d*$_5$, 136489-96-8; acetophenone-*2,3,4,5,6-d*$_5$, 28077-64-7; benzaldehyde-*2,3,4,5,6-d*$_5$, 14132-51-5; 2,4,6-triphenyl-d_{15}-pyrylium tetrafluoroborate, 136489-99-1; 2,4,6-triphenyl-d_{15}-nitrobenzene, 136489-97-9; 2,4,6-triphenyl-d_{15}-aniline, 136489-98-0.

Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

---

(19) Main, P.; Fiske, S. E.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. MULTAN80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England, and University of Louvain, Belgium, 1980.

(20) Busing, W. R.; Martin, K. O.; Levy, H. S. ORFLS, Oak Ridge National Laboratory Report, ORNL-TM-305, 1965.