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FACTORS AFFECTING STABILITY AND EQUILIBRIA OF FREE RADICALS—IX[1,2]

NON-EQUIVALENCE OF ARYL GROUPS IN 1,1-DIARYL-2-BENZENESULPHONYL-HYDRAZYLS AND RELATED COMPOUNDS

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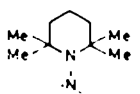
Abstract—1,1-Bis-(3',5'-di-*t*-butylphenyl)-2-benzenesulphonyl-hydrazine **11** and the corresponding 2-picryl-hydrazine **13** were synthesized. Oxidation of **11** afforded the stable hydrazyl **12** whose ESR spectrum could be simulated in terms of three hyperfine coupling constants. These experimental data leave no alternative but to assign larger proton hyperfine coupling constants to one aryl group in **12** than to the other. This non-equivalence was interpreted in terms of the Linnett theory. The picrylhydrazyl **14** does not give completely resolved ESR spectra. Structures were ascertained by IR, UV-vis, ^{1}H NMR and ^{13}C NMR spectra.

INTRODUCTION

Stable hydrazyls, **1**, like diphenylpicrylhydrazyl (DPPH), may be considered as a special class of "push–pull" aminyls **2**,[3] with the strongest neutral donor group R_2N. This type of stabilization, examined theoretically by Dewar in 1952,[4] has only recently received increased attention, and was named by Katritzky as "merostabilization";[5] reviews[1,6,7] now have to consider not only aromatic (R = Ar), but also aliphatic hydrazyls,[8,9] such as **3**,[9] which owes its stability (as opposed to persistence[8,10]) in solution, only to merostabilization, since its ESR spectra clearly show couplings only to the two nitrogen atoms.

$R_2N\text{–}\dot{N}\text{–}$Acceptor   Donor–$\dot{N}$–Acceptor

1   **2**



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High-resolution ESR spectra of DPPH and of related triaryl-hydrazyls (with 2,6- or 2,4-dinitrophenyl as acceptor)[11] are too complicated for a detailed analysis of coupling constants. Some progress was made by ENDOR experiments[12] and by theoretical calculations of spin density in DPPH.[13] We followed a different approach, analyzing ESR spectra of molecules possessing fragments of DPPH, e.g. diphenyl-arenesulphonyl-hydrazyls[14] and picryl-alkoxy-aminyls,[15,16] in which acceptor arenesulphonyl groups introduce no coupling constants in ESR spectra, and donor alkoxy groups like methoxy introduce only one coupling constant. Alternatively, one may modify the hydrazyl molecule **1** in order to reduce the number of coupling constants, using cyano,[17] 2,4,6-tricyanophenyl,[3,18] 2,4,6-tricarbomethoxyphenyl,[3,18] trifluoromethanesulphonyl,[19] or arenesulphonyl as acceptor groups and 1,1-di-(*p*-bromophenyl)-amino[14] as a donor group.

These investigations, and particularly the ESR spectra of 1,1 - diphenyl - 2 - arenesulphonylhydrazyls,[14] 1,1 - di - (*p* - bromophenyl) - 2 - arenesulphonylhydrazyls[14] and 1 - cyano - 2,2 - diphenylhydrazyl[17] revealed an unexpected feature, the two geminal aryl groups were magnetically non-equivalent. However, the ESR spectra were still relatively line-rich so that the simulation of the ESR spectrum, which gives absolute credibility to the assignment of ESR hyperfine coupling constants, was not possible.

The aim of the present investigation was to further simplify the ESR spectrum up to the point where comparison between simulated and experimental ESR spectra became possible. We therefore synthesized a 1,1-diarylhydrazine devoid of protons *meta* to nitrogen, thereby suppressing the two smallest coupling constants in the corresponding hydrazyl.

RESULTS AND DISCUSSION

1,1 - Bis - (3',5' - di - t - butylphenyl) - 2 - benzenesulphonylhydrazine **11** *and the corresponding picrylhydrazine* **13**

The synthesis is outlined in formulae **4–11**: 3,5 - di - *t* - butylaniline **7**,[20] was converted into the diarylamine **8**, and hence into the 1,1 - diaryl - 2 - benzenesulphonylhydrazine **11** using known reactions.

In the ^{1}H NMR spectra of 3,5 - di - *t* - butyl - toluene **5** and 3,5 - di - *t* - butylaniline **7**, the *p*-protons appear at lower field than the *o*-protons, in 3,5 - di - *t* - butylbenzoic acid **6**, or 3,5 - di - *t* - butylnitrobenzene (the

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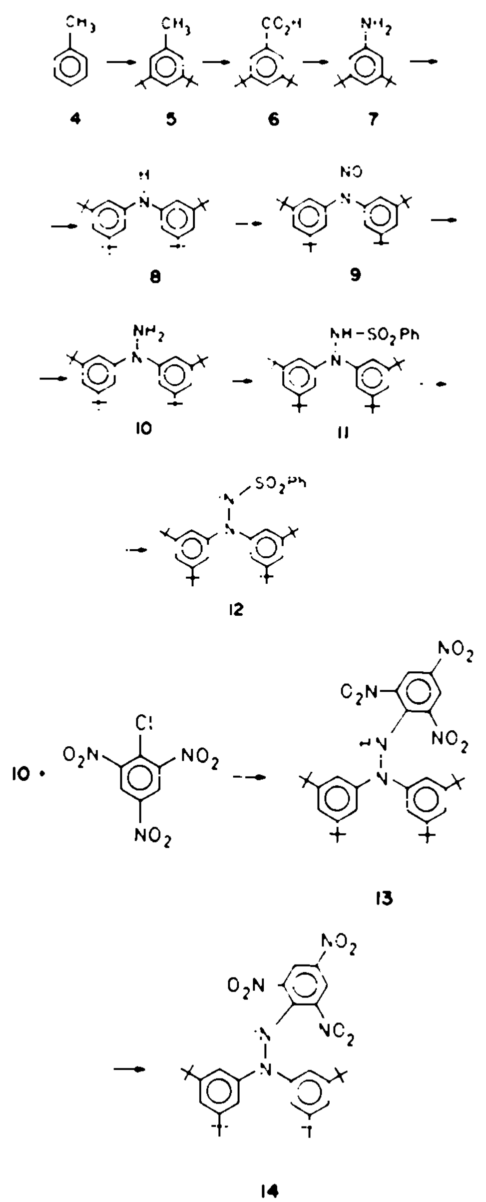

latter to be reported in a separate paper) this order is reversed, in agreement with theory. These *o*- and *p*-protons are degenerate in the ^1H NMR spectra of the diarylamine **8** and diarylhydrazine **10**. They are distinct, however, in the nitrosoamine **9** and in the sulphonylhydrazine **11**; owing to restricted rotation around the N–N bond in the nitrosoamine at room temperature, the two aryl groups give distinct NMR signals both in the ^1H NMR and in the ^{13}C NMR spectrum. All assignments for the ^1H and ^{13}C NMR spectra (see Experimental) were substantiated by decoupling experiments, by deuteration to establish NH peaks (^1H NMR) and by off-resonance experiments (^{13}C NMR).

In the ^1H NMR spectrum of the picrylhydrazine **13**, the *m*-picryl protons appear non-equivalent and broadened at room temperature. This agrees with ^1H NMR data on other picrylhydrazines obtained by Heidberg, Weil, Janusonis and Anderson, who determined Arrhenius activation energies of 12–15 kcal/mole for rotation around the N-picryl bond.[21]

1,1 - *Bis* - (3',5' - *di* - t - *butylphenyl*) - 2 - *benzenesulphonylhydrazyl* **12** *and its ESR spectrum*

On oxidizing hydrazine **11** with lead tetraacetate or with lead dioxide in benzene, a violet solution was obtained (λ_{max} 502 nm) which contained hydrazyl **12**. The colour is due to a well-defined absorption band at 502 nm, similar to that of DPPH. The radical **12** is stable in deaerated benzene for a few days at room temperature. The ESR spectrum of the deaerated benzene solution presents 42 lines (Fig. 1, upper spectrum).

The "stick-diagram" of the experimental spectrum, i.e. the measured lengths of first-derivative lines, shows a clear 1:2:3:2:1 pattern expected for a hydrazyl with similar coupling constants for the two nitrogens. The centres of the submultiplets are indicated in Fig. 2. Considering the outer lines of the first submultiplet, where no overlap exists with neighbouring submultiplets, it is apparent that the submultiplet must have 10 lines. There are few theoretical possibilities for such a submultiplet with equidistant lines due to six protons, and they were all obtained from a computer program,[22,23] and printed[21] up to 15 equidistant lines. Examining this list, only two possibilities have to be taken into consideration since only these are due to six protons and lead to an intensity ratio of inner lines, to the outmost smallest line, higher than 10:

$$\text{one } a_H = 3d,\ \text{one } a_H = 2d,\ \text{four } a_H = 1d \qquad \text{(i)}$$

$$\text{three } a_H = 2d,\ \text{three } a_H = 1d. \qquad \text{(ii)}$$

where *d* is the interval between two adjacent equidistant lines. Neither of these possibilities is compatible with magnetically equivalent aryl groups. The second set (ii) could be refined to allow simulation of the experimental ESR spectrum (Fig. 1, lower spectrum) with only three hyperfine coupling constants: two nitrogen atoms with $a_N = 9.25$ gauss, three hydrogens with $a_H = 2.23$ gauss, and three hydrogens with $a'_H = 1.40$ gauss.† The half-width of each line in the simulated spectrum was 0.8 gauss. The coupling to *t*-butyl protons was smaller than this value.

The agreement between experimental and simulated spectra is quite satisfactory and leaves no doubt about the assignment. The slight intensity differences may be due to a small difference between the two nitrogen hyperfine splitting constants. To determine these a_N values unambiguously, radical **12** would have to be synthesized with ^{15}N in one, then in the other position.

The experimental result thus indicates two equal nitrogen coupling constants, as in most hydrazyls,[5-9] as well as three smaller and three larger hydrogen coupling constants. It can be easily seen that it is impossible to obtain equivalent aryl groups with these six a_H and a'_H values. It is well known that in most aromatic free radicals, *ortho*- and *para*-hydrogens have almost equal coupling constants. Therefore the most logical distribution of the six proton coupling constants is as indicated in Fig. 1, three $a_H = 2.23$ gauss to one aryl group, and three $a'_H = 1.40$ gauss to the other aryl.‡

We want to stress that this result is not due to any artificial hypothesis, but is the direct, compelling, con-

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†One gauss = 10^{-4} Tesla units.

‡From the experimental spectrum it is impossible to determine which aryl has the larger and which one the smaller coupling constant. On the formula, the aryl *syn* to the arenesulphonyl group was arbitrarily assigned the larger coupling constants.

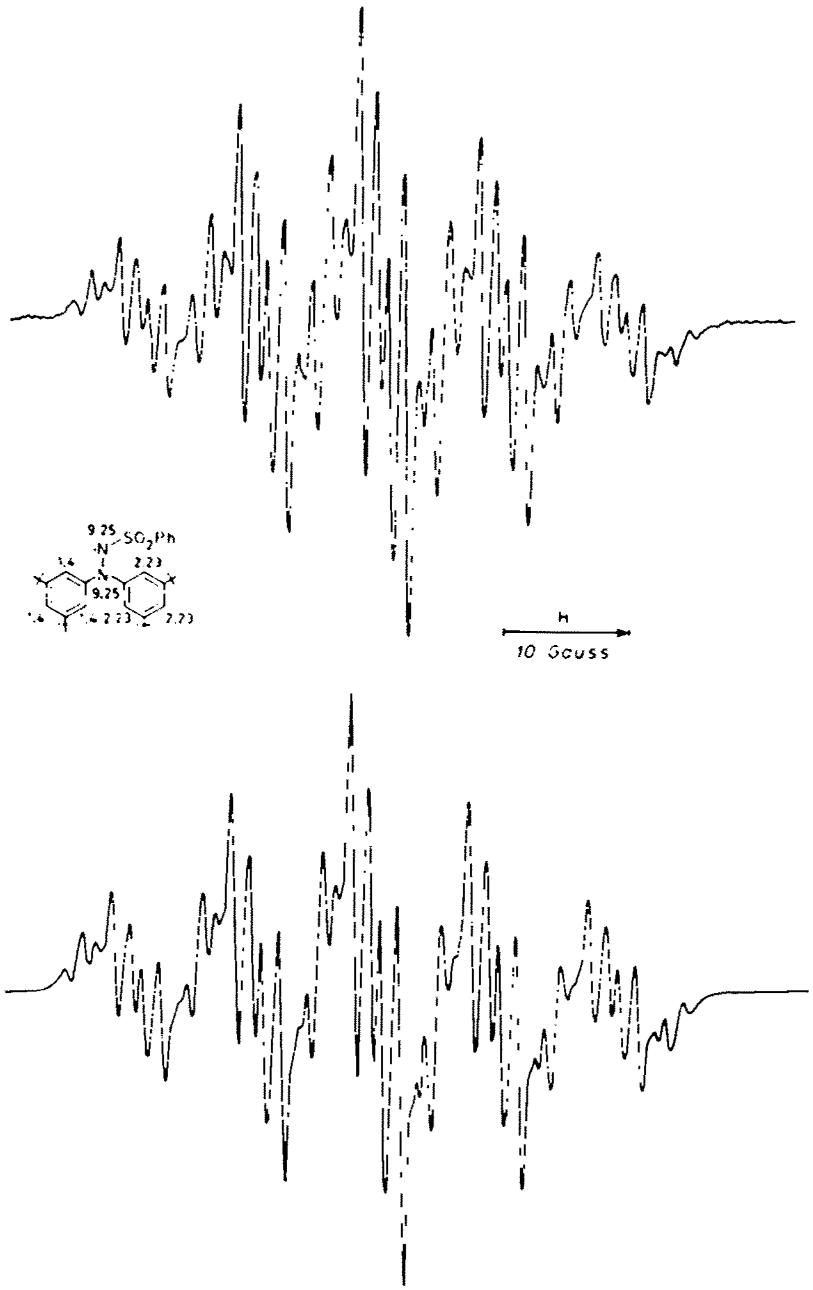
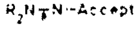


Fig. 1. First-derivative ESR spectrum of radical **12** in benzene: experimental above, simulated below.

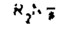
sequence of the experimental ESR spectrum. Thus the non-equivalence of aryl groups in 1,1-diarylhydrazyls with an acceptor group bonded to nitrogen-2, is an experimentally established fact.

The origins of this non-equivalence are open to speculation. In the crystal, DPPH has geometrically non-equivalent phenyl groups (both in angles and in bond lengths),[24] but there may be other factors involved (packing, donor-acceptor interactions with solvent molecules in the crystal). However, we are interested in permanent interactions which act in solution. The simplest interpretation is to postulate an increased bond order between the two nitrogens in hydrazyls (in agreement with X-ray data[24]), leading to restricted rotation around this bond, and to the appearance of *syn-anti* non-equivalence. The origin of this increased bond order is the spin delocalization, manifest in the equal a_N-hyperfine coupling constants. This delocalization is best described by Linnett's theory,[25] according to which all atoms in hydrazyls **15** (analogously in aminoxyls **16**) have complete octets of electrons with paired spins α and β if and only if the N–N and N–O bonds are intermediate between a single and a double bond, according to formulae **15** and **16**.



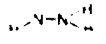
$R_2\dot{N}\overset{\cdot}{\underset{\cdot}{-}}\dot{N}-\text{Acceptor}$

15



$R_2\dot{N}\overset{\cdot}{\underset{\cdot}{-}}\dot{O}$

16



17

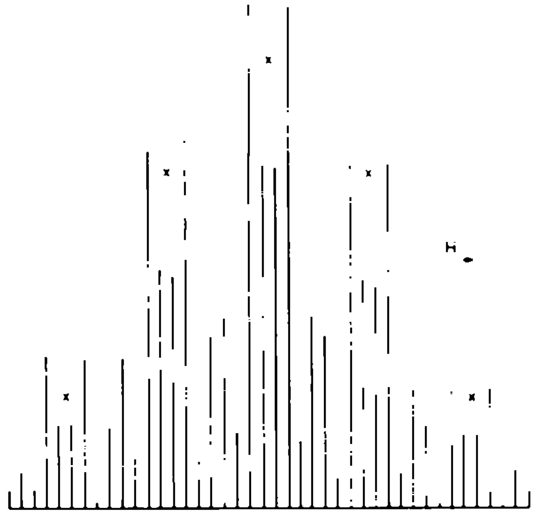


Fig. 2. Stick diagram representation of the experimental ESR spectrum of **12**.

Theoretical calculations by M. Raban lead to high rotation barriers around the N–N bond in **17**: it prefers the eclipsed conformation and the rotation barrier is 46 kcal/mole using CNDO/2' or 37 kcal/mole using INDO.[26] The corresponding anion is staggered in the ground state and has quite low barriers (10 kcal/mole) while the cation has an eclipsed ground state conformation and a very high barrier, 74 kcal/mole.[26] In agreement with these calculations, the ESR spectrum of **12** does not change appreciably in the temperature range −40 to +80° in various solvents.

As a more general conclusion, the magnetic non-equivalence between the two aryl groups in radical **12** should be a general phenomenon in all hydrazyls **1** or **15**, including DPPH. So far, neither theoretical calculations[11] nor interpretations of ENDOR experiments[12] have taken this non-equivalence into account.

1,1 - *Bis* - (3',5' - *di* - t - *butylphenyl*) - 2 - *picrylhydrazyl* **14** *and its ESR spectrum*

As in the ESR spectrum of DPPH, under normal recording conditions, only the splitting due to the two hydrazinic nitrogen atoms appears in the ESR spectrum of **14**, which presents five broad lines with a spacing of 9 gauss (Fig. 3). A spectrum with higher resolution is difficult to obtain, and its number of lines is too high and imprecise to allow an exact assignment of hyperfine coupling constants.

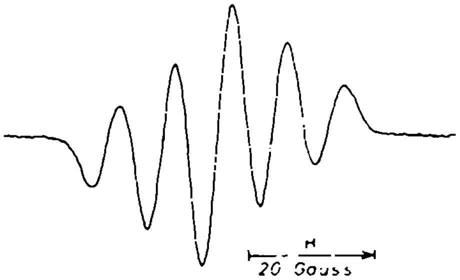


Fig. 3. ESR spectrum of radical **14** in benzene under medium resolution.

Mass spectra of **8**, **10** and **11** present parent peaks at *m/e* 393, 408 and 548, respectively, and common peaks at *m/e* 322, 189, 181.5, 167.5 and 147 (**11** also has M—SO_2 at 484 a.m.u.), in agreement with structure.

EXPERIMENTAL

Instrumentation. IR spectra were recorded with Zeiss-Jena UR-10 instruments, UV-visible spectra with an Optica (Milan) CF-4 instrument, ^1H NMR spectra with a Varian A-60A instrument, ^{13}C NMR spectra with a Varian CFT-20 instrument and ESR spectra with a Varian E-12 spectrometer. The simulated ESR spectra were recorded with a Varian Spectrosystem 100 data processing system[33] consisting of a Varian Data 620/i computer connected on-line with an ESR Varian E-12 spectrometer.

3,5-*Di*-t-*butylaniline* **7** was prepared according to literature methods from toluene **4**. This was *t*-butylated with *t*-BuCl and $AlCl_3$ to 3,5 - di - *t* - butyltoluene, **5**, m.p. 31–32°,[27-30] ^1H NMR spectrum in CCl_4: τ 8.71 (18H, s, *t*-Bu), 7.70 (3H, s, Me), 3.18 (2H, d, *o*-H), 3.06 (1H, t, *p*-H), $J_{o,p}$ 1.8 Hz. IR spectrum (KBr): 712 s, 865 s, 900 m, 1211 m, 1258 s, 1372 s, 1404 m, 1490 s, 1614 s cm^{-1}. Oxidation with potassium permanganate in pyridine afforded 3,5 - di - *t* - butylbenzoic acid **6**, m.p. 173°;[31,32] ^1H NMR spectrum in CCl_4: τ 8.61 (18H, s, *t*-Bu), 2.39 (1H, t, *p*-H), 2.04 (2H, d, *o*-H), −2.85 (1H, s, COOH). IR spectrum (KBr): 710 s, 782 m, 900 s, 1275 s, 1618 m, 1710 vs cm^{-1}. Schmidt degradation converted this acid into 3,5 - di - *t* - butylaniline, 7, m.p. 54°.[20] ^1H NMR in CS_2: τ 8.76 (18H, s, *t*-Bu), 6.67 (2H, s, NH_2), 3.67 (2H, d, *o*-H), 3.33 (1H, t, *p*-H), $J_{o,p}$ 1.8 Hz. IR spectrum (KBr): 710 s, 855 s, 1260 s, 1339 b, 1379 s, 1410 m, 1450 m, 1500 s, 1620 s, 3400 m, 3480 m.

3,3',5,5'-*Tetra*-t-*butyl-diphenylamine* **8**, was obtained from 3,5 - di - *t* - butylaniline (22.6 g, 110 mmol) and its hydrochloride (24.2 g, 100 mmol) which were heated at 260° in a Carius tube for 20 h. The product was crushed and extracted with benzene. The filtered benzenic solution was washed twice with 1N HCl, then with water, dried ($MgSO_4$), and evaporated, leaving 3,3',5,5' - tetra - *t* - butyl - diphenylamine which was purified by two recrystallizations from ethanol, yield 25 g, 58%, m.p. 117° in agreement with literature data.[34] (Found: C, 85.47; H, 11.15; N, 3.42. Calc. for $C_{28}H_{43}N$: C, 85.43; H, 11.01; N, 3.56%). ^1H NMR in $CDCl_3$: τ 8.68 (36H, s, *t*-Bu), 4.40 (1H, broad, NH), 3.03 (6H, narrow multiplet, ArH). IR spectrum (KBr): 711 s, 733 m, 860 s, 905 m, 998 m, 1008 s, 1040 m, 1133 m, 1210 m, 1253 s, 1315 s, 1335 vs, 1370 m, 1398 m, 1440 vs, 1484 m, 1538 w, 1595 vs, 2864 m, 2900 m, 2960 vs, 3340 m, 3395 m (the last two bands are replaced in CCl_4 by one band at 3445 cm^{-1}).

N,N - *Bis* - (3,5 - *di* - t - *butylphenyl*) - *nitrosoamine* (3,3',5,5' - *tetra* - t - *butyl* - *diphenylnitrosoamine*), **9**, was obtained from the above diarylamine (39.4 g, 100 mmol) in 750 ml ethanol with 10 ml conc. HCl; under stirring, the solution was treated at 0–5° with 6.9 g (100 mmol) sodium nitrite dissolved in 10 ml water and 20 ml ethanol. After 1 h at 0–5° the solution was diluted with 100 ml water. The precipitated colourless nitrosoamine was filtered off, washed with dilute ethanol and dried. Yield 40.5 g; 96%, m.p. 108° (from ethanol). (Found: C, 79.0; H, 10.0; N, 7.2. $C_{28}H_{42}N_2O$ requires: C, 79.50; H, 9.95; N, 6.64%). ^1H NMR spectrum of IX in $CDCl_3$: τ 8.68 and 8.67 (18H each, s, *t*-Bu), τ 3.10 (2H, d, *o*-H) coupled to 2.50 (1H, t, *p*-H) and τ 2.74 (2H, d, *o*-H) coupled to 2.61 (1H, t, *p*-H), $J_{o,p}$ 1.8 Hz. ^{13}C NMR spectrum in $CDCl_3$: δ 31.4 (12C, *t*-Bu), 35.1 (4C, *t*-Bu), 113.7 and 121.6 (2 *o*-C each), 120.7 and 123.1 (1 *p*-C each), 136.7 and 1424 (2 *m*-C each), 152.0 and 152.5 (1 arom. N–C each). IR spectrum (KBr): 705 s, 782 s, 809 w, 841 m, 870 s, 893 w, 905 m, 1080 vs, 1188 m, 1208 w, 1254 s, 1280 w, 1301 w, 1340 w, 1370 s, 1400 w, 1440 s, 1485 m, 1500 vs, 1600 s, 1610 s, 2865 s, 2900 s, 2960 vs.

On heating above the m.p., **9** evolves gas bubbles and resolidifies to another compound whose structure is under investigation.

1,1 - *Bis* - (3',5' - *di* - t - *butylphenyl*) - *hydrazine*, **10**. The nitrosoamine (4.23 g, 10 mmol) in 75 ml ethanol with 7 g (100 mmol) zinc powder was treated dropwise with 12 g acetic acid at 20–25° (immersed thermometer) during 1 h with efficient stirring and external cooling. The mixture was stirred for 1–2 h until a sample no longer gave blue colour on dilution with conc. HCl. The mixture was filtered off, and the filtrate was combined with two warm ethanolic washings. Water (15 ml) was added; the crystals of zinc acetate which frequently appear in the filtrate went into solution and the asym. diarylhydrazine crystallized. It was filtered off, washed with water and recrystallized from benzene–petroleum ether, or from ethanol. It presents two crystalline forms, m.p. 126° with resolidification and then m.p. 145°. The product recrystallized from ethanol presents only the latter m.p. Yield 85–90%. (Found: C, 82.29; H, 10.96; N, 6.89. $C_{28}H_{44}N_2$ requires: C, 82.38; H, 10.78; N, 6.84%). The hydrazine **10** is sensitive to sunlight which converts it rapidly into a lemon-yellow compound. ^{1}H NMR spectrum of **10** in $CDCl_3$: τ 8.69 (36H, s, *t*-Bu), 5.81 (2H, broad, NH_2), 2.89 (6H, narrow multiplet, ArH). ^{13}C NMR spectrum in $CDCl_3$: δ 31.5 (12C, *t*-Bu), 35.0 (4C, *t*-Bu), 113.9 (4 *o*-C), 115.9 (2 *p*-C), 151.5 (4 *m*-C), 148.9 (2 arom. N–C). IR spectrum (KBr): 711 s, 720 w, 796 m, 821 m, 846 vs, 860 s, 875 m, 895 w, 905 w, 930 vw, 1014 w, 1042 w, 1122 w, 1136 m, 1210 s, 1253 vs, 1336 vs, 1370 s, 1400 w, 1439 vs, 1487 s, 1605 vs, 2865 s, 2900 s, 2960 vs, 3350 m cm^{-1} (in CCl_4 the last band appears at 3434 cm^{-1}, with a weaker band at 3356 cm^{-1}).

1,1 - *Bis* - (3',5' - *di* - t - *butylphenyl*) - 2 - *benzenesulphonylhydrazine*. **11**. The above asym. diarylhydrazine (4.1 g, 10 mmol) in 10 ml benzene was refluxed for 10 h with 0.88 g (0.64 ml, 5 mmol) freshly distilled benzenesulphonyl chloride. After 24 h standing, the deposited crystals were filtered off and recrystallized from benzene–petroleum ether, or from ethanol. Yield 2.1 g, 77%, m.p. 204°C (Found: C, 74.15; H, 9.02; N, 4.88; S, 5.08. $C_{34}H_{48}N_2O_2S$ requires: C, 74.41; H, 8.81; N, 5.11; S, 5.84%). ^{1}H NMR spectrum in $CDCl_3$: τ 8.80 (36H, s, *t*-Bu), 3.10 (4H, d, *o*-H), 2.93 (2H, t, *p*-H), 2.75 (broad, NH), 2.1–2.7 (5H, m, phenyl-H); $J_{o,p}$ 1.8 Hz. IR spectrum (KBr): 588 vs, 619 w, 685 m, 710 m, 730 s, 754 m, 862 s, 880 m, 900 w, 910 m, 1010 m, 1030 w, 1042 m, 1075 vw, 1098 s, 1170 vs, 1188 w, 1210 w, 1254 m, 1312 m, 1331 s, 1348 vs, 1370 m, 1400 w, 1422 w, 1458 s, 1488 m, 1600 vs, 2870 s, 2905 s, 2960 vs, 3240 vs (in CCl_4 the last band appears at 3234 cm^{-1} with a weaker band at 3320 cm^{-1}).

1,1 - *Bis* - (3',5' - *di* - t - *butylphenyl*) - 2 - *picrylhydrazine*. **13**. The above asym. diarylhydrazine (2.05 g, 5 mmol) in 50 ml ethanol was treated with 1.05 g (12.5 mmol) $NaHCO_3$ and 1.24 g (5 mmol) picryl chloride for 2 h at 50–60°, then refluxed for 15 min. Chloroform (50 ml) was added into the hot solution which was then filtered. This solution was washed twice with 50 ml portions of water, and the chloroform layer was concentrated in vacuum to 10 ml. Ethanol (15 ml) was added and the solution was left overnight. The deposited violet prisms were filtered off and recrystallized from chloro–ethanol or from benzene–petroleum ether. Yield 2.95 g, 98%, m.p. 175°C. (Found: C, 65.75; H, 7.35; N, 11.23. $C_{34}H_{45}N_5O_6$ requires: C, 65.89; H, 7.32; N, 11.30%). ^{1}H NMR spectrum in $CDCl_3$: τ 8.71 (36H, s, *t*-Bu), 3.04 (4H, d, *o*-H), 2.73 (2H, t, *p*-H), $J_{o,p}$ 1.8 Hz, τ 1.45 (1H, broad, *m*-H), 0.85 (1H, broad, *m*-H) and −0.20 (1H, s, NH). Prominent bands in the IR spectrum (KBr): 1302 s, 1340 vs, 1600 vs, 1624 s, 2970 vs, 3295 s cm^{-1}; in CCl_4 the last band appears at 3305 cm^{-1}.

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