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MAGNETOCHEMISTRY OF FREE RADICALS—II

THE SELWOOD EFFECT, REAL OR IMAGINARY?

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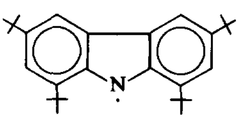
Abstract—Static magnetic-susceptibility measurements on powder samples of the stable free radicals 1,3,6,8-tetra-t-butyl-carbazolyl (77–343 K; 56%), bis-(4-methoxyphenyl)-nitroxyl (77–400 K; 99.7%), and 3-t-butyl-1,5-diphenyl-verdazyl (77–343 K; 98.1%) are described. The results are interpreted in terms of a non-existing "Selwood effect"—an invalidation of the measured results due to a large diamagnetism in free radicals.

Twenty-five years ago, Selwood and Dobres[1] on the basis of their own magnetic measurements made some critical remarks on the determination of the magnetic susceptibility of free radicals according to the static method of Gouy. As already discussed,[2] the correct determination of the diamagnetic correction (which according to Selwood cannot be correct in principle, "Selwood effect") is a prerequisite for the use of the method of Gouy. The whole problem may be summarized in the following question: Does a free, resonance-stabilized radical exhibit exactly 50% of the diamagnetism of the corresponding diamagnetic dimer or is its diamagnetism higher? Two methods can be used to answer this question.

(1) The radical content of a paramagnetic specimen is determined according to Gouy. The same specimen is then subjected to another method of measurement which does not require a diamagnetic correction, i.e. which gives only the value of the paramagnetism (e.g. ESR). When both methods reveal the same value, a "Selwood effect" is not involved.

(2) For non-associated radicals there is a simpler solution of the problem: If the method of Gouy reveals 100% radical content for the specimen of a resonance-stabilized radical, the "Selwood effect" is precluded as it would lower the radical content considerably. This second method of checking if a "Selwood effect" is present can only be applied to highly stable radicals which can be prepared in pure, solid form. Thus, careful and clean preparation of the radicals or the corresponding H compounds is a prerequisite of this method.

Since the "Selwood effect", which is derived from the additional delocalization of the single free electron, should be strongest in the case of a planar radical, we investigated 1,3,6,8-tetra-t-butyl-9-carbazolyl (**1**); according to Neugebauer and Fischer,[3] this radical has a plane structure and is not associated.



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On the basis of hydrogenation experiments, Neugebauer found the radical content of **1** to be 94%. We prepared radical **1** from 1,3,6,8-tetra-t-butylcarbazole (**2**) which, in turn, was prepared from carbazole, t-butyl chloride, and aluminum chloride according to a modified literature procedure[4] and which was then subjected to extensive purification procedures, the yields of **2** being 15–85%.

Magnetic measurement of solid **2** revealed a magnetic susceptibility of $\chi_{\text{mol}}^{-} = -296.26 \times 10^{-6}$. This value is in excellent accordance with the value calculated according to Haberditzl[5] (-298.40×10^{-6}). The correction for the diamagnetic portion of the susceptibility of **1** is calculated from the experimental value, yielding, after subtraction of an N–H increment, a susceptibility of $\chi_{\text{mol}}^{-} = -294.46 \times 10^{-6}$.

Compound **2** was converted to the anion by treatment with butyllithium in benzene solution under an argon atmosphere, and the anion oxidized with 1 equivalent of iodine to give the deep-blue radical **1**.[3] Purification of the crude product was carried out by fractional crystallization from n-pentane (Uvasol). However, radical **1** always crystallizes together with the carbazole **2** and cannot be obtained in pure form by this method. In general, the second crystal fraction shows the highest radical content as can be seen from the NH absorption of **2** at 3520 cm^{-1} in the IR spectrum. The specimen with the highest radical content had m.p. 144–146° (lit.[3] m.p. 144–145°).

The magnetic measurement of the specimen with the highest radical content was performed between 77 and 343 K. The radical content is independent of temperature; the mean value from 10 measurements of the moment μ_1 ($\mu_1 = 2.828 \times \sqrt{(\chi_{\text{mol}} \times T)}$) is 1.292 Bohr magnetons (BM). This corresponds to 74.6% of the theoretical value and to a radical content of 55.6%.

Contrary to earlier measurements,[4,†] the Curie temperature of **1** was found by us to be $\theta = 0°$ in all measurements. When the earlier data are also referred to $\theta = 0°$, the radical content decreases from *ca.* 105 to 85† and from 95 to 77%,[4] respectively. This is in better agreement with the experimental findings, since also Neugebauer[3] could not eliminate the impurity responsible for the NH absorption.

Although radical **1** is monomeric according to the facts discussed above, it is so unstable in solution that it partially decomposes upon attempted purification and can thus not be obtained in absolutely pure form, and accordingly not be used for the examination of the "Selwood effect".

We therefore abandoned the condition of coplanarity and examined twisted radicals of sufficient stability,

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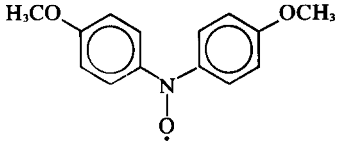
†Magnetic measurements were carried out by Y. Deguchi (radical concentration at 77 K: 104.8%; $\theta = -18°$).[6]

although their possible "Selwood effect" was expected to be smaller. A carbon radical of this type, 100% pure perchlorotriphenylmethyl, has already been described; however, it does not exhibit a "Selwood effect".[2b]



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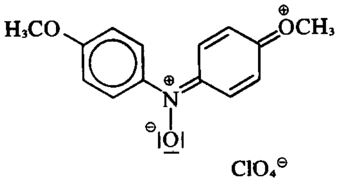

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A further example was chosen from the class of the aromatic nitroxyls: bis[4-methoxyphenyl]nitroxyl (**3**) which, since its synthesis by Meyer and Billroth[7] is one of the most intensely studied stable radicals. The earliest magnetic measurements in the thirties afforded strongly different results. Meanwhile, the accuracy of the magnetic balances has been considerably improved. Regarding the fact that in early studies radical contents of 93 and 115% had been found[8] and that in more recent work a maximum radical content of only 97% could be reached, remeasurement of **3** with the magnetic balance was indicated.

The starting material for the synthesis of **3** was di-*p*-anisyl-oxoammonium perchlorate (**4**). This compound was prepared by reaction of anisole with nitrating acid in glacial acetic acid according to Meyer and Billroth[7a] and subsequent addition of perchloric acid. The yield of **4** was 10%. The original procedure[7a] had to be modified in terms of standardization of narrow temperature intervals and mode of addition of the reagents in order to obtain reproducible yields. The purification procedure described[7a] which involves recrystallization from acetone/ligroin could not be reproduced by us. We therefore used the crude product (*ca.* 50% **4**) for the preparation of radical **3**.

Since the diamagnetic H-compound of **3** is not stable and since the perchlorate **4** could not be purified, the amount of diamagnetism of **3** had to be calculated. According to earlier measurements,[9] the diamagnetism of **4** could anyhow not be used. This is evident from the fact that the quinonoid system of **4** is not present in radical **3** and thus the values of the diamagnetism of **3** and **4** must be different.

Calculation according to Pascal[10] of the diamagnetic portion of the susceptibility of **3** yields $\chi^{-}_{\text{mol}} = -151.02 \times 10^{-6}$. The more exact calculation according to Haberditzl cannot be performed because one of the bond increments is not known.

The quinonoid perchlorate **4** was smoothly reduced to radical **3** with zinc powder in acetone;[7] repeated recrystallization gave the pure radical; m.p. 153.5–154° (lit.[9] m.p. 153°). The solid radical **3** was measured on the magnetic balance in the temperature range of 82–403 K (Table 1).

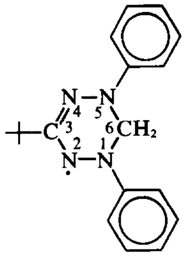
The mean value from all measurements of the magnetic moment $\mu_2 (\mu_2 = 2.828 \times \sqrt{(\chi^{+}_{\text{mol}} \times (T - \theta)})$ is 1.728 BM which corresponds to 99.8% of the theoretical value. The actual radical content is correspondingly 99.7%. The Curie temperature was found to be $\theta = -5°$, which is in agreement with earlier measurements ($\theta = 0$ to $-13°$).

Table 1. Magnetic measurements of radical 3

T[K]	$\chi^{+}_{\text{mol}} \times 10^6$ Found	$\chi^{+}_{\text{mol}} \times 10^6$ Calc.	μ_2[B M]	% Radical
82.0	4404	4312	1.751	102.1
143.2	2516	2531	1.727	99.4
162.7	2210	2237	1.722	98.8
182.5	1972	2001	1.720	98.6
208.5	1744	1757	1.726	99.3
229.0	1598	1603	1.729	99.7
249.6	1467	1474	1.728	99.5
270.1	1362	1364	1.731	99.9
290.4	1266	1270	1.729	99.7
324.1	1137	1140	1.730	99.7
325.3	1134	1136	1.731	99.8
337.5	1091	1095	1.729	99.6
358.1	1029	1033	1.729	99.6
380.0	977	974	1.734	100.3
400.9	925	924	1.733	100.1

The found radical content of 99.7% proves that radical **3** can be obtained in completely pure form and precludes the "Selwood effect" for **3** with certainty.

As a further nitrogen radical we measured 3-t-butyl-1,5-diphenyl-verdazyl (**5**). We used a specimen of **5** with m.p. 109–109.5° and the corresponding non-radical N-methyl derivative 6-t-butyl-2,4-diphenyl-5-methyl-2,3,4,5-tetrahydro-1,2,4,5-tetrazine (**6**, m.p. 88.5–89°).[11]



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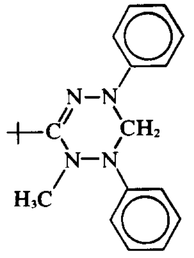

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As the diamagnetism of **5** can only be calculated with rough approximation it was established experimentally via measurement of the diamagnetic reference compound **6**. The result was $\chi^{-}_{\text{mol}} = -187.61 \times 10^{-6}$. Subtraction of the CH_3 portion (calculated according to Pascal[10]) yields the following value for the diamagnetic correction:

$$\chi^{-}_{\text{mol}} = -172.82 \times 10^{-6}.$$

Magnetic measurements of the solid radical **5** were carried out in the temperature range 77–344 K. The data obtained are listed in Table 2.

The mean value from all measurements of the magnetic moment is 1.715 BM, which corresponds to 99% of the theoretical value. The actually measured radical content is 98.1%, however. The Curie temperature was $\theta = 0°$. The radical deficiency of 2% lies within the accuracy of the magnetic measurement. An eventual "Selwood effect" can at most be of this order of magnitude.

In summary, on the base of our investigation and the work of Theilacker[12] and Zimmermann[13] it can be concluded that the "Selwood effect" exists only in theory

Table 2. Magnetic measurements of radical **5**

T[K]	$\chi^{+}_{mol} \times 10^6$ Found	$\chi^{+}_{mol} \times 10^6$ Calc.	μ_1[B M]	% Radical
77.0	4875	4872	1.733	100.1
153.8	2368	2439	1.707	97.1
174.1	2110	2155	1.714	97.9
194.3	1894	1931	1.716	98.1
213.5	1719	1757	1.713	97.8
233.8	1573	1605	1.715	98.0
256.0	1438	1465	1.716	98.2
276.2	1340	1358	1.720	98.7
289.3	1270	1297	1.714	97.9
295.5	1241	1270	1.713	97.7
308.4	1188	1216	1.712	97.7
323.0	1135	1161	1.712	97.8
343.6	1068	1092	1.713	97.8

and that in practice it does not invalidate the values of the susceptibility of all hitherto measured (by the Gouy method) radicals which were unambiguously proven to be pure. Apparently, Selwood was led to the postulation of his "effect" due to insufficiencies in the preparation of the substance specimen used. Thus, the magnetic balance may also in the future be used for the quantitative determination of radical contents.

EXPERIMENTAL

1,3,6,8-*Tetra-t-butyl-carbazole* (**2**). To a suspension of carbazole (16.7 g; 0.1 mol) in t-BuCl (112.0 g; 1.2 mol) at 25° powdered $AlCl_3$ (13.5 g; 0.1 mol) was added portionwise (every 5–10 min) over a period of 60–90 min. After addition of each portion of $AlCl_3$, the mixture was shaken until the $AlCl_3$ had been used up (slackening of foaming and evolution of HCl). The mixture was coloured dark brown to black, and the carbazole gradually dissolved. After 24 hr at 25°, the solidified mixture was decomposed by 300 ml ice water and extracted with 500 ml ether. The ether phase was washed 3 times with excess water, dried with Na_2SO_4, and evaporated *in vacuo* to yield a redbrown, strongly fluorescent, viscous oil. This oil was dissolved in petroleum ether (60–80°) and the soln was filtered through silica gel columns (2–4 times) until these were no longer black. The pale yellow oil thus obtained was dissolved in boiling EtOH to produce a yellowish crystal pulp on cooling. The crude product was 3 times crystallized from EtOH to give a white amorphous material of m.p. 193.5–194.5°. The soln in petroleum ether again was filtered through a column of silica gel, then the material was recrystallized from EtOH yielding 6.0–33.0 g (15–85%) colourless crystals, m.p. 191.5–192.5° (lit.[4] m.p. 191–192°).

The compound crystallizes in 2 different modifications, showing the same TLC–^{1}H-NMR (CCl_4): $\delta = 1.46$ ppm (s, 2 tBu), 1.59 (s, 2 tBu), 7.30 (d, J = 2 Hz, 2=CH), 7.84 (d, J = 2 Hz, 2=CH), 7.98 (s, NH); MS (70 eV): Found 391.3232, ($C_{38}H_{41}N$) requires: 391.3239. In order to prepare a powdered sample suitable for magnetic measurement, a boiling soln of **2** in EtOH was cooled very slowly while stirring vigorously. After drying for 6 hr at 50° and 0.005 Torr over silica gel/P_2O_5, the sample was used directly.

1,3,6,8-*Tetra-t-butyl-carbazolyl* (**1**). The sample was prepared from **2** (7.8 g; 0.02 mol) according to Neugebauer.[3] All operations were performed in O_2-free solvents under argon. The crude blue tarry material was dissolved quickly in about 60 ml warm pentane. Upon cooling with ice water, a first crop of **1** crystallized. The crystals were filtered off under argon using a glass frit. The filtrate was cooled to −80° and a second crystal fraction was collected under argon and washed with a very small amount of pentane. N_2 was blown vigorously through the material on the frit for about 1 hr in order to remove traces of solvent from the crystals. The dried crystals were powdered under argon in a Schlenk-flask using a glass rod. The powder obtained was used for magnetic measurements: 2.9 g (37%), m.p. 144–146° (lit.[3] m.p. 144–145° (dec)).

Di-(4-methoxyphenyl)-oxoammonium perchlorate (**4**). The preparation following Meyer and Billroth[7a] only succeeded when the temp. was kept at 25–30° and the mixture strongly sitrred during HNO_3-addition within 20 min. At the beginning of the reaction, 1 drop of HNO_3 was added every 15 sec. After addition of 0.4–0.6 ml of HNO_3, the temp. suddenly increased very rapidly. The reaction flask had to be immersed in an ice-NaCl bath within 5 sec to stop the temp. rise at 30°. After this, every 8 sec one drop of HNO_3 could be added. 1.5–1.7 g of crude **4** were obtained; the purification of this product failed.

Bis[*4-methoxyphenyl*]*nitroxyl* (**3**). Crude **4** (2.0 g) was used to prepare **3** according to Meyer and Reppe.[7b] The highly impure **3** was first crystallized from EtOAc at 50–60°. The brown-black crystals thus obtained were purified by precipitation from the acetone soln with ice water repeatedly until the initially black solution became orange-red (4–6 times). The purified **3** was dissolved in warm MeOH and precipitated with water to form tiny needles, which were crystallized twice from warm EtOAc: 0.4 g (56%) brilliant brown-red plates, m.p. 153.5–154° (lit.[9] m.p. 153° (dec)). (Found: C, 68.88; H, 5.81; N, 5.82. $C_{14}H_{14}NO_3$ requires: C, 68.84; H, 5.78; N, 5.73%). After 6 hr drying at 40°/0.005 Torr over silica gel/P_2O_5, radical **3** was powdered in an agate mortar to be suitable for magnetic measurement.

Magnetic measurements. The susceptibility determinations were done by the Gouy technique on powder samples of about 300–600 mg in fields of 9.4, 8.4 or 7.3 kOe. The details of the apparatus are described elsewhere.[14]

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