Tetrahedron Letters, Vol. 22, No. 15, pp 1455 - 1458 ,1981
Printed in Great Britain

0040-4039/81/151455-04$02.00/0

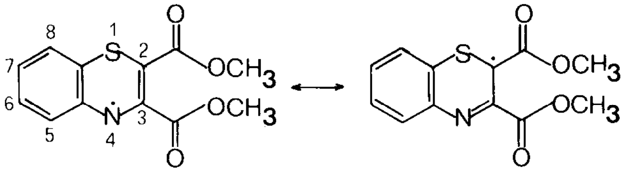
A PERSISTENT 1,4-BENZOTHIAZINYL RADICAL

Francesco Ciminale*
Istituto di Chimica Organica, Facoltà di Scienze, 70126 Bari,Italy.
Gaetano Liso and Giuseppe Trapani
Istituto di Chimica Organica, Facoltà di Farmacia, 70126 Bari,Italy.

Abstract. ESR characterisation of a "capto-dative" stabilised 1,4-benzothiazinyl radical is reported.

Oxidation of phenothiazines by various oxidising systems has been extensively studied and the cation and the neutral radicals involved in such processes have been characterised by ESR spectroscopy[1-4]. Analogous species from 1,4-benzothiazines, which are expected to be less stable owing to the reduced extent of conjugation in the π-system, have not been detected so far. However, some of us have previously invoked a benzothiazinyl radical to explain the behaviour of differently substituted benzothiazines on autoxidation[5,6].

In the present report we give ESR evidence for the spontaneous formation of a persistent neutral radical II from the 2,3-dimethoxycarbonyl-4H-1,4-benzothiazine I[7].



(a) (b)

II

Solution of I in $CHCl_3$, immediately after preparation, gave an ESR spectrum consisting of a broad 1:1:1 triplet due to the nitrogen splitting (a=4.90G). This resonance gradually became more intense and at the same time each triplet component exhibited a complex hyperfine structure. The spectrum of Figure 1a was recorded after *ca.* 2 hours and remained unchanged for a very long time (several days). Analysis of this spectrum, reported below, appears straightforward for radical II. However, further unequivocal support to such an identification was successfully achieved upon generating the suspected radical by methods which have been found to afford neutral radicals from related systems[2,3]. Thus, when I was treated in vacuum with dimethyl sulfoxide-acetic anhydride or with a benzene solution of diphenylpicrylhydrazyl (DPPH), spectra similar to 1a were obtained.

The complex hyperfine structure of spectrum 1a was analysed with the aid of the simpler resonance observed in $CHCl_3$ from the corresponding perdeutero-

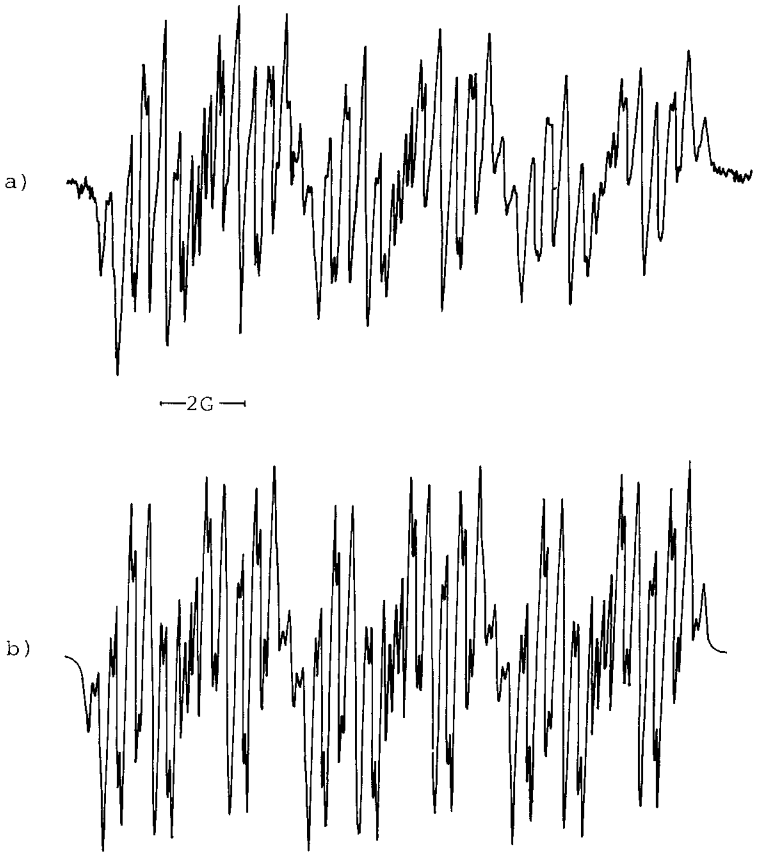


Figure 1. ESR spectrum of radical **II**: (a) observed; (b) simulated with a line-width of 0.21G.

dimethoxy derivative[8] wherein three proton coupling constants are easily measured besides the nitrogen splitting: 1.80, 1.18 and 0.3G. An excellent computer simulation (Figure **1b**) of spectrum **1a** was therefore obtained on the basis of the following hyperfine splitting constants: $a^N=4.87$, $a^H_5=1.80$, $a^H_7=1.19$, $a^H_8=0.28$, $a^H_6=0.12$, $a^H_{CH_3}=0.41$G (quartet). The methyl coupling can be undoubtedly assigned to the carbomethoxy at C-2 which is the only capable of conjugatively participating in the unpaired electron delocalisation.

Proton-assignments are consistent with spin densities calculated by the McLachlan[9] modification of the HMO method. The parameters we have utilised for the nitrogen and the sulfur are those suggested by Gilbert *et al.*[1] for the phenothiazinyl radical: $h_N=0.8$, $k_{CN}=1.0$; $h_S=1.25$, $k_{CS}=0.57$. As far as the carbomethoxy groups are concerned, parametrisation has been made by analogy with the radical anion of dimethyl phthalate[10]: $h_{\dot{O}}=1.5$, $k_{C=O}=1.6$; $h_{\ddot{O}}=2.0$, $k_{C-O}=0.8$. Furthermore, according to this model, the resonance integral of the ring-carbomethoxy bond was assumed to be $k_{CC'}=\beta\cos\theta$, where θ is the angle by which each ester group would be twisted with respect to the heterocyclic nucleus as a consequence of the steric hindrance exerted by the adjacent substituent. While the carbomethoxy at C-2, contributing to the hyperfine pattern, was assumed to be cooplanar ($\theta=0°$) with the rest of the molecule, different values of θ were tested for the carbomethoxy at C-3. The results which best match the experimental data, reported in the Table, were obtained for $\theta=90°$, that is for the carbomethoxy at C-3 not contributing to the π-system.

Table. Calculated and Experimental Spin Densities for Radical **II**.

position	ρ_{calcd}	ρ_{exptl}^{a}
2	0.334	-
4	0.306	0.295
5	0.071	0.067
6	-0.014	(-)0.004
7	0.067	0.044
8	-0.020	(-)0.010

[a] Calculated from experimental coupling constants using the following Q-values[1]: $Q^{H}=-27$, $Q^{N}=16.5G$.

Compared to the phenothiazinyl radical[1], the species **II** shows smaller aromatic protons and nitrogen splitting constants and a larger g-value (2.0062). These trends are in agreement with the fact that, in the radical **II**, a considerable fraction of the spin density is localised on the C-2 (see Table) bearing a carbomethoxy substituent. In terms of valence bond structures, this situation is conveniently interpreted by the limiting structure **IIb**, where the stabilising effect due to a "capto-dative" substitution[11] of the radical centre appears particularly evident.

Acknowledgment. We thank Dr. A. Alberti (CNR, Ozzano Emilia - Bologna) for spectrum simulation.

References

1) M.F.Chiu, B.C.Gilbert and P.Hanson, J.Chem.Soc.(B), 1700(1970).
2) Y.Tsujino, Tetrahedron Lett., 4111(1968).
3) C.Jackson and N.K.D.Patel, Tetrahedron Lett., 2255(1967).
4) G.Cauquis, A.Derouzier and D.Serve, J.Electroanal.Chem., **47**, 193(1973)

5) V.Carelli, F.Micheletti Moracci, F.Liberatore, M.Cardellini, M.G.Lucarelli, P.Marchini, G.Liso and A.Reho, *Int.J.Sulfur Chem.*, **8**, 267(1973).

6) P.Marchini, G.Trapani, G.Liso, V.Berardi, *Phosphorus and Sulfur*, **3**, 309(1977).

7) Synthesis of I has been already reported: G.Liso, G.Trapani, V.Berardi and P.Marchini, *J.Heterocyclic Chem.*, **17**, 377(1980).

8) This compound was prepared from the dimethyl(d_6) acetylenedicarboxylate following the method described in reference 7.

9) A.D.McLachlan, *Molec.Phys.*, **3**, 233(1960).

10) M.Hirayama, *Bull.Chem.Soc.Jap.*, **40**, 2234(1967).

11) L.Stella, Z.Janousek, R.Merényi and H.G.Viehe, *Angew.Chem.,Int.Ed.Eng.*, **17**, 691(1978) and references cited therein.

(Received in UK 16 January 1981)