Tetrahedron Letters No. 7, pp 571 - 574, 1972. **Pergamon Press. Printed in Great Britain.**

1,2-BIS-BENZENESULPHONYL-1,2-DIETHOXYHYDRAZINE AND ITS TEMPERATURE-DEPENDENT PROTON MAGNETIC RESONANCE SPECTRUM

Alexandru T. Balaban and Alice Vasilescu

Institute of Atomic Physics, P. O. B. 35, Bucharest, Roumania

(Received in UK 17 December 1971; accepted for publication 13 January 1972)

Within the framework of a systematic approach to stable free radicals, it was conjectured [1] that additional stabilization of nitrogen free radicals occurs whenever bulky acceptor and donor groups are bonded to the same nitrogen atom. Examples of such free radicals are 1,1-diphenyl-2-picrylhydrazyl (I), alkoxy-picryl-aminyl (II) [2] and 1,1-diphenyl-2-benzenesulphonylhydrazyl (III).[3] In order to test whether alkoxy-benzenesulphonyl-aminyl free radicals (IV), the missing combination in the above enumeration, could be stable, we investigated the oxidation of N-ethoxy-benzenesulphonamide (V). Although it resulted that the dimer VI of IV does not yield IV on heating but decomposes instead losing N_2, interesting facts emerged from this research.

$2,4,6\text{-}(O_2N)_3C_6H_2\text{-}\dot{N}\text{-}NPh_2$

I

$2,4,6\text{-}(O_2N)_3C_6H_2\text{-}\dot{N}\text{-}OAlk$

II

$PhSO_2\text{-}\dot{N}\text{-}NPh_2$

III

$PhSO_2\text{-}\dot{N}\text{-}OAlk$

IV

Ethoxyamine hydrochloride [4] (0.1 mole) was treated with 0.1 mole sodium ethoxide in ethanol,[5] and the solution of ethoxyamine was treated with benzenesulphonyl chloride (40 mmoles). The filtered solution was evaporated to dryness in vacuum, and by repeated extractions with ether which was subsequently distilled off, N-ethoxy-benzenesulphonamide (V) was obtained, m. p. 57° (from cyclohexane). IR spectrum (KBr) : ν SO_2 1168, 1340 ; ν Ph 1485, 1590 ; ν NH 3215 cm^{-1}. NMR spectrum ($CDCl_3$) : CH_3 triplet τ 8.90, CH_2 quadruplet τ 6.08, J = 7 Hz, Ph multiplet and NH at τ 2.9 - 1.9.

No stable free radicals were detected by ESR on oxidizing solutions of V with PbO_2 or $Pb(OAc)_4$. Treatment of V in acetone with $KMnO_4$ at 45° followed by addition of aqueous CH_2O for removing excess $KMnO_4$, filtration and precipitation with water afforded 1,2-bis-benzenesulphonyl-1,2-diethoxyhydrazine (VI), colourless crystals m. p. dec. 74° (from benzene - petroleum ether or from ethanol - water without heating). IR spectrum (KBr) : ν SO_2 1188, 1375 ; ν Ph 1483, 1590 cm^{-1} ; no ν NH. Conservation of crystalline VI for a few hours at 25° causes sudden spontaneous decomposition in a vigorous exothermal reaction leading to several products which are being investigated.

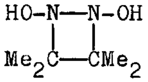
Very few analogues of VI with O-N-N-O bonds are known : the 1,2-dihydroxy-diazetidine VII was recently reported.[6] Acyclic 1,2-diacylhydrazines VIII exhibit temperature-dependent NMR spectra.[7]

$PhSO_2$-NH-OEt

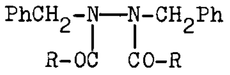
V

EtO-N(SO_2Ph)-N(SO_2Ph)-OEt

VI



VII

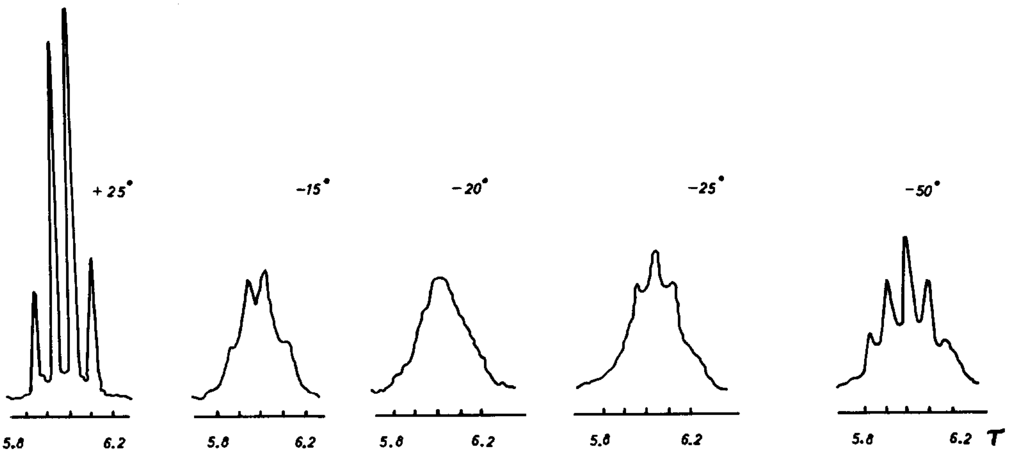


$PhCH_2-N(COR)-N(COR)-CH_2Ph$

VIII

The NMR spectrum of VI, determined with a Tesla instrument at 80 MHz, is also temperature-dependent. In $CDCl_3$ at room temperature, it has the CH_3 triplet at τ 9.02, CH_2 quadruplet at τ 6.02, J = 7 Hz, and Ph multiplet at τ 2.5-1.9. On cooling, the 1:3:3:1 CH_2 quadruplet coalesces at -20° and reappears as a 1:4:6:4:1 quintuplet at lower temperatures (figure), indicating either two equally populated non-equivalent kinds of ethyl groups, or anisochronous methylene protons with the marginal lines of the AB quadruplets too weak to be discernible. With $\Delta\nu = 6.6$ Hz at the coalescence temperature an energy barrier of 13 ± 1 kcal/mole is calculated.

Compound VI is at the same time a hydrazine and a hydroxylamine derivative. From the rich literature on derivatives of hydrazine [7,8] or hydroxylamine [9] which present anisochronous groups [10] owing to restricted (i) nitrogen inversion,[11] (ii) rotation around N-O bonds [12] or oxygen inversion, or (iii) rotation around N-N bonds,[12] it appears that all these processes may contribute to the measured energy barrier.



REFERENCES

1. A. T. Balaban, *Rev. Roumaine Chim.* **16**, 725 (1971).

2. A. T. Balaban, M. Frangopol, N. Negoita, P. T. Frangopol and M. Paraschiv, *Rev. Roumaine Chim.* **14**, 941 (1969).

3. A. T. Balaban and N. Negoiţa, paper submitted to *Tetrahedron*.

4. J. R. Nicolaus, L. Mariani and E. Testa, *Ann. Chim.* (*Rome*), **53**, 281 (1963) ; M. Torigore, *Chem. Pharm. Bull.* (*Japan*), **9**, 613 (1961).

5. L. Horner and A. Christmann, *Chem. Ber.* **96**, 388 (1963).

6. P. Singh, D. G. B. Boocock and E. F. Ullman, *Tetrahedron Letters*, 3935 (1971).

7. G. J. Bishop, B. J. Price and I. O. Sutherland, *Chem. Commun.* 672 (1970).

8. J. E. Anderson, D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.* **91**, 6371 (1969) ;

   M. J. S. Dewar and W. B. Jennings, *ibid.* **91**, 3655 (1969) ; *Tetrahedron Letters*, 339 (1970) ;

   T. T. Bopp, M. D. Havlicek and J. W. Gilje, *J. Amer. Chem. Soc.* **93**, 3051 (1971) ;

   C. H. H. Bushweller and J. W. O'Neil, *ibid.* **92**, 2159 (1970).

9. D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.* **87**, 4089 (1965) ;

D. L. Griffith, B. L. Olson and J. D. Roberts, *ibid*. **93**, 1646 (1971) ;

B. J. Price and I. O. Sutherland, *Chem*. *Commun*. 1070 (1967) ;

R. E. Banks, M. G. Barlow, R. N. Haszeldine and M. K. Mc Creath, *J*. *Chem*. *Soc*. 7203 (1965) ;

M. Raban and G. W. J. Kenney Jr., *Tetrahedron Letters*, 1295 (1969) ;

W. Walter and E. Schaumann, *Liebigs Annalen Chem*. **747**, 191 (1971) ;

R. L. Powell, T. Posner and C. D. Hall, *J*. *Chem*. *Soc*. (B) 1246 (1971).

10. Y. Shvo, E. C. Taylor, K. Mislow and M. Raban, *J*. *Amer*. *Chem*. *Soc*. **89**, 4910 (1967) ;

K. Mislow and M. Raban, *Topics in Stereochemistry*, **1**, 1 (1967) ;

M. L. Martin and G. J. Martin, *Bull*. *Soc*. *Chim. France*, 2217 (1966) ;

M. Van Gorkom and G. E. Hall, *Quart*. *Rev*. **22**, 14 (1968) ;

T. H. Siddall and W. E. Stewart, *Progress in NMR Spectroscopy*, **5**, 33 (1969).

11. J. M. Lehn, *Fortschr*. *Chem*. *Forsch*. **15**, 311 (1970).

12. J. P. Lave, *Progress in Physical Organic Chemistry*, **6**, 1 (1968).