Tetrahedron Letters No. 21, pp. 1797-1798, 1971. Pergamon Press. Printed in Great Britain.

ON THE CYCLOPROPYL CONJUGATION IN BENZO[a]SPIRO[2,5]OCTA-1,4-DIENE-3-ONE[1)]

P. Rys, P. Skrabal and H. Zollinger

Department of Industrial and Engineering Chemistry,

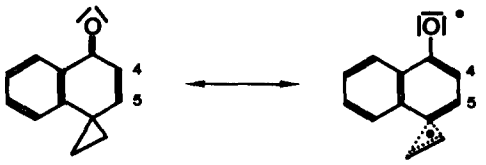
Swiss Federal Institute of Technology (ETH),

Zurich

(Received in UK 22 March 1971; accepted in UK for publication 19 April 1971)

The recent paper on aromaticity via cyclopropyl conjugation by Clark and Fiato[2)] prompts us to report on the electronic structure of the title compound 1. It was prepared for comparison with Winstein's spiro[2,5]octa-1,4-diene-3-one (2)[3)] and spiro[anthrone-10,1'-cyclopropane] (3)[4)].

The NMR spectrum of 1 in $CDCl_3$ shows a multiplet at 1.71 ppm for the cyclopropyl protons. Similar chemical shifts were reported for these protons in 2 (1.69 ppm, singlet, in $CDCl_3$) and 3 (1.84 ppm, singlet, in $CDCl_3$). These chemical shifts are about 1 ppm downfield from the absorption of the cyclopropyl protons in saturated spiranes. It is well established that the protonated cyclopropyl spirodienones 2 and 3 exist as static bridged systems in which the charge delocalisation extends over the cyclopropane rings[5)]. In our opinion the chemical shifts of the unprotonated species must be interpreted in terms of a contribution of aromatic forms (e.g. symbolized by 1b) to the ground state of the molecules[6)].



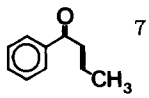
1a 1b

The multiplet for the two pairs of nonequivalent cyclopropyl protons of 1 in $CDCl_3$ becomes a singlet in CD_3OD and is shifted to 1.82 ppm. The protons in positions 4 and 5 which are equivalent in $CDCl_3$ (singlet at 6.48ppm) show a quartet ($J_{4,5}$=9cps) at 6.59 ppm in CD_3OD. Both changes can be explained by a bigger contribution of the mesomeric form 1b which assumes more importance in the more polar solvent. In 1b all four cyclopropyl protons are exposed to the magnetic field induced by the diamagnetic ring current in naphthalene and may therefore become equivalent. The protons H_4 and H_5 may become nonequivalent because they become aromatic protons in a position ortho to a positive and negative substituent.

In addition, the electronic spectrum of 1 resembles more to that of a naphthalene derivative than to the spectrum of a cross conjugated ketone (see Table 1).

The tendency of the protonated species to add nucleophiles under ring opening decreases in the order 2 > 1 > 3. This is in accordance with the expected stability of these species.

Table 1. Electronic spectra

	λ_{max} (log ε)	solvent
1	282(4.36), 329(4.05), 336(sh)	$CHCl_3$
	225(4.11), 258(4.14), 310(3.90)	C_2H_5OH
 7)	256(4.24)	C_2H_5OH
1-naphthol[8]	233(4.52), 295.5(3.71), 323(3.43)	C_2H_5OH

REFERENCES

1) The title compound was synthesized in the course of the Ph.D. thesis of R. Vogelsanger, ETH, 1970.
2) R.A. Clark and R.A. Fiato, J. Amer. Chem. Soc. 92, 4736 (1970).
3) R. Baird and S. Winstein, ibid. 85, 567 (1963).
4) L. Eberson and S. Winstein, ibid. 87, 3506 (1965).
5) See for example: J.W. Pavlik and N. Filipescu, Chem. Commun.[London] 1970, 765.
6) For a more detailed discussion see Ref. 2).
7) R.P. Mariella and R.R. Raube, J. Amer. Chem. Soc. 74, 521 (1952).
8) C. Daglish, ibid. 72, 4859 (1950).