Tetrahedron Letters, Vol.22, No.36, pp 3545 - 3548, 1981
Printed in Great Britain

0040-4039/81/363545-04$02.00/0

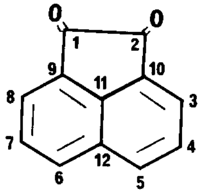
PROTONATION OF ACENAPHTHOQUINONE. A NOVEL PERIPHERAL 10 π-ELECTRON AROMATIC SYSTEM

Daniel Bruck*[1], Abraham Minsky, Arie Dagan and Mordecai Rabinovitz
Department of Organic Chemistry, The Hebrew University of Jerusalem
Jerusalem 91904, Israel

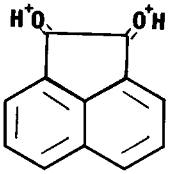
Abstract: *Acenaphthoquinone (1) undergoes protonation to afford the respective double protonation product 2. The proton and carbon NMR parameters of 2 are discussed.*

Among the medium size 10 π-electron systems, the eleven membered conjugated non-bridged Huckeloid cation is the only missing link.[2] Other members of the series are $C_8H_8^{-2}$ [3], $C_9H_9^{-1}$ [4,5], bridged [10][6], annulene and its higher homolog the [11] annulenyl cation[2] which are by now milestones in the exciting area of non-benzenoid aromatics. However, in the eleven membered ring systems there is a steric factor which does not allow to prepare the non-bridged hydrocarbon and its derived cation. To overcome the inherent steric hindrance of these systems Vogel synthesized the bridged ten and eleven-membered 10π-electron systems[2,5]. Acenaphthoquinone (1) provides a non-alternant peripheral eleven membered system perturbed by a triply linked carbon at its center. Such a system should in principle form a 11C-10π conjugated planar cation. Protonation of 1 can occur on the two carbonyl oxygens to afford 2. If more than just a stabilization of the two positive charges may be involved e.g. by the formation of a 10 π-electron system then this must include a delocalization of one positive charge over the 11C framework and localization of the second positive charge at the bridgehead carbons preferably carbon-11 viz. structures 3 or 4. The stabilizing power of the hydroxy groups as well as the bridgehead carbons[7] should play an important role in the preparation of 11C-10π system.

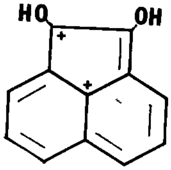
We wish to report our results on the protonation of acenaphthoquinone (1), a suitable substrate for the preparation of a bridged [11] annulenyl dication (2)[8]. ^1H NMR (DMSO-d_6) of acenaphthaquinone (1) gives rise to three bands in the proton spectrum (DMSO-d_6, downfield relative to HMS) 8.63 (d, J=8Hz, 2H), 8.28 (d, 2H, J=8 Hz), 8.11 ppm (t, 2H, J_1=8 Hz, J_2=2 Hz) assigned to protons at positions 3, 4 and 5 respectively.



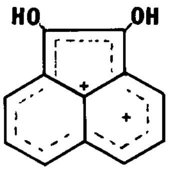
1



2



3



4

In SbF_5-FSO_3H 1:1M solutions in SO_2 only two bands were detected δ ppm = 8.51 (t, 2H, J=9 Hz), 9.14 (t, 4H, J_1=9 Hz, J_2=2 Hz) for an ABC type spectrum with partial overlapping of A and B proton bands. The relatively low field aromatic proton shifts indicate a highly positive charge distribution in the "naphthalene" perimeter. The aromatic protons of diprotonated para-diacetyl benzene appear at δ = 8.86 ppm while diprotonated naphthalene-1,8-dicarboxylic acid anhydride, shows two triplets in the aromatic region at 8.42 and 7.85 ppm. A similar low field shift has also been observed in other doubly protonated benzene derivatives[9]. The inability to detect the -OH band of protonated acenaphthoquinone resembles other hydroxy substituted aromatic systems[10], and is due to a fast exchange with the environment.

The protonation was also studied by ^{13}C NMR spectroscopy. This spectroscopy is expected to give an even better indication concerning the location of charges in molecules. In the proton decoupled ^{13}C NMR spectrum (SO_2ClF relative to TMS at 24°C) acenaphthoquinone gives rise to seven bands. The chemical shifts are given in Table 1. Assignment of the bands is based on their relative intensities and chemical shifts.

Our results show that the protonation causes a large effect on most carbon chemical shifts. Carbon atoms at position 3, 4 and 5 are deshielded due to a partial positive charge. (all of them are positively charged due to the fact that it is a non-alternant system. However, carbons C-3 and C-8 are more influenced than carbon atoms C-5, C-6, C-4 and C-7 respectively, indicating the relative charge distributions at these positions. Comparison of the ^{13}C NMR spectra with the singly charged, protonated acenaphthenone prepared by Olah[8]

Table 1. Carbon Chemical Shifts of Acenaphthoquinone and its Protonate

Carbons[a]	quinone[b] in SO_2ClF	Protonated quinone [c]	Difference Δδ
C- 1,2	194.00	181.40	+12.60
C- 3,8	129.97	146.80	-16.83
C- 4,7	118.96	132.22	-13.26
C- 5,6	125.90	137.10	-11.20
C- 9,10	121.53	116.39	+5.14
C- 11	129.70	164.10	-34.40
C- 12	128.10	130.80	-2.70

a) We could not distinguish between carbon atoms C-3,8 and C-5,6. b) Relative to TMS (DMSO taken as 40.78 ppm relative to TMS). (c) Protonation was achieved by means of SO_2ClF-SbF_5-FSO_3H solution at -30°C, chemical shifts are from TMS, calculated using the value of 204.3 ppm for the carbonyl carbon of acetone-d_6 which served as a reference in capillary (Bruker WH-300, acetone-d_6 lock).

demonstrates that an entirely different pattern of charge distribution has been obtained. Most striking is the downfield shift of the bridgehead carbon C-11 indicating a localized positive charge at this point which is in agreement with the assumption on the stability gained by the whole system when one positive charge is localized. The highfield shift of carbons C-1 and C-2 is rationalized by the formation of a partial carbon-carbon double bond rather than the C=O bond of the parent compound. This rationalization explains the highfield shift of carbons 9, 10 and 12 as well. The small effect on carbon atom 12 indicates no significant positive charge delocalization on this carbon.

From the NMR data it seems that the protonation of acenaphthoquinone in Sb_5F-FSO_3H 1:1M in SO_2 leads to a diprotonated species (4) which can be rationalized in terms of an aromatic positively charged 11C-10π electron system, in which one charge is delocalized along the perimeter and one charge is localized on carbon atom C-11.

REFERENCES AND NOTES

1. Present address: Makteshim Chemical Works, P.O.Box 1, Beer Sheva, Israel.
2. The bridged system has been reported: W. Grimme, H. Hoffman and E. Vogel, Angew. Chem., Int. Ed., 4, 354 (1965).
3. T.J. Katz, J. Am. Chem. Soc., 82, 3785 (1960).
4. E.A. LaLancette and R.E. Benson, J. Am. Chem. Soc. 85, 1941 (1965).
5. T.J. Katz and P.J. Garratt, J. Am. Chem. Soc. 85, 2852 (1965).
6. E. Vogel, Israel J. Chem. 29, 1 (1980); ibid. 87, 5194 (1964) and references cited therein.
7. B.M. Trost and P.L. Kinson, J. Am. Chem. Soc., 97, 2438 (1975).
8. The singly-charged 1-acenaphthenium ion and derivatives as well as the singly charged protonated acenaphthene were prepared by G.A. Olah, G. Liang and P. Westerman, J. Am. Chem. Soc. 95, 3698 (1973).
9. e.g. Doubly protonated dimethyl phthalate and phthalic acid: D. Bruck, Ph.D. thesis, presented to the Hebrew University of Jerusalem, 1976.
10. K.H. Harmon in "Carbonium Ions", G.A. Olah and P. v. R. Schleyer Ed., Wiley-Interscience, 1973, Vol. IV, pp. 1622.

(Received in UK 29 June 1981)