

CCA-841

YU ISSN 0011-1643

539.19:516

Original Scientific Paper

## Graph Theory and Molecular Orbitals. XIII. On the Stability of Annelated Tropylium Cations\*

I. Gutman and N. Trinajstić\*\*

Theoretical Chemistry Group, Institute »Ruđer Bošković«, 41000 Zagreb, Croatia, Yugoslavia, and Theoretical Chemistry Department, University of Oxford, Oxford OX1 3TG, England

Received May 27, 1974

A topological approach is used for studying the origin of differences in stabilities of benzoannelated, and furo- and/or thienoannelated tropylium cations. Recently available experimental data could be thus rationalized and the  $pK_{R+}$  values of yet unknown compounds in these series predicted.

Several research groups have established quite clearly that benzoannelation leads to destabilization<sup>1-3</sup> whereas furo- and/or thienoannelation<sup>\*\*\*</sup> stabilizes<sup>4-6</sup> the tropylium cation (1). This has been demonstrated by the considerable change in the experimental  $pK_{R+}$  values which occurs as a result of the annelation of tropylium cations. The formulae of various annelated tropylium cations and their  $pK_{R+}$  values, where these are available, are listed in the Figure.

Despite some previous theoretical work<sup>3-10</sup>, no satisfactory scheme for rationalizing these experimental findings has, it seems<sup>11</sup>, yet been proposed.

In the last few years, a set of simple rules has been derived<sup>12-19</sup> for predicting various properties of conjugated systems, these rules being purely based on inspection of the topology of the given molecule<sup>20-23</sup> (that is to say a way in which atoms making up a particular molecule are connected). In the present work we show that this *topological approach* is an appropriate one for understanding and systematizing data such as that given in the Figure. In particular we should like to go some way towards answering the following questions:

(i) Why does benzoannelation decrease so drastically the stability of the tropylium cation?

(ii) Why are the stabilities of known furo- and/or thienoannelated tropylium cations only slightly different?

(iii) Why are the effects of benzoannelation, and furo- and/or thienoannelation so different?

\* Part XII: I. Gutman, B. Ruščić, N. Trinajstić, and C. F. Wilcox, Jr., *J. Chem. Phys.*, in press

\*\* Permanent address: Institute »Ruđer Bošković«, 41000 Zagreb, Croatia, Yugoslavia

\*\*\* A fusion of a furan and/or thiophene ring with their b-sides onto the tropylium ion.

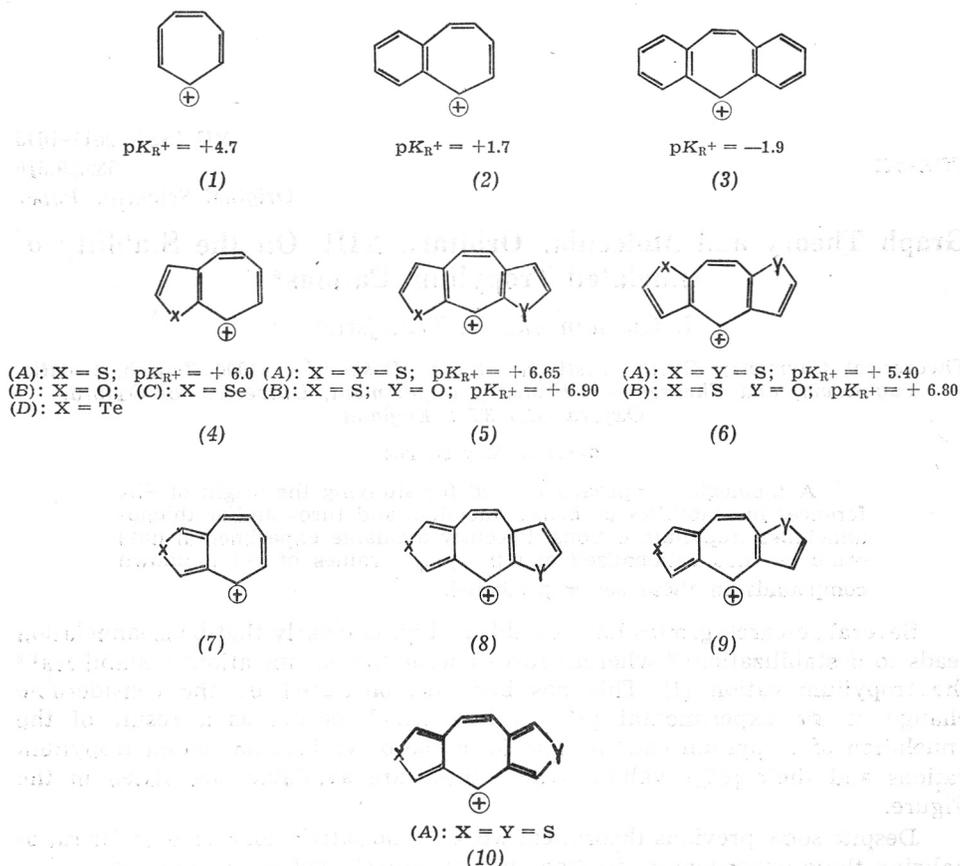
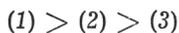
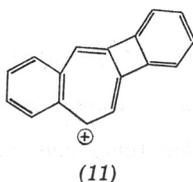


Figure — Annelated tropylium cations

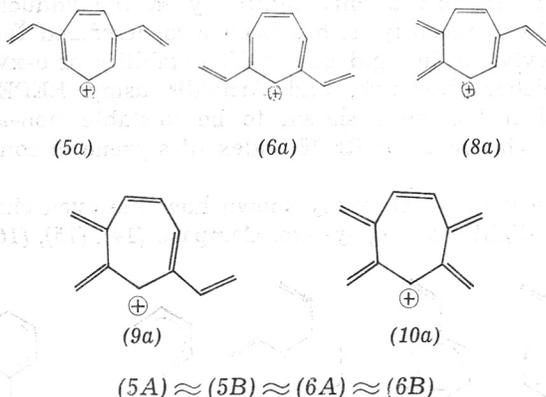
We try first to answer question (i). In our recent work<sup>17</sup> we derived several rules which apply directly to this case, which we summarize here: annelation of an alternant moiety to a molecule qualitatively decreases the redox ability of the  $\pi$ -electron system. With this in mind we can immediately predict the stability order of the benzoannelated tropylium ions:



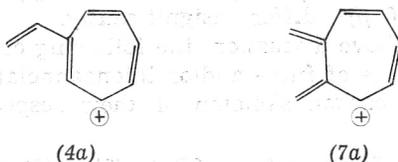
which, of course, parallels the experimental findings<sup>1-3</sup>. Similarly, this pattern is also well fitted by the observations of Garratt and Vollhardt<sup>24</sup>, who found that the  $pK_{R^+}$  value (-1.3) of (11) differs considerably from that of the tropylium cation.



Let us now consider question (ii). We have recently demonstrated<sup>25-27</sup> that the stability order of a series of heterocyclic conjugated isomers (containing  $[\sigma + \sigma]$  — bivalent heteroatoms) may be predicted by considering only the topology of the »parent hydrocarbons« — *i. e.* the hydrocarbon obtained by »removing« the heteroatoms. A similar idea has also recently been proposed by Watson and Warren<sup>28</sup>. If we now inspect the carbon skeleton of the isomeric molecules (5), (6), (8)—(10), we can immediately note several points; firstly, there is essentially no difference between (5a) and (6a), and thus the prediction

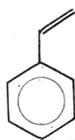


is readily made and it is fully in agreement with experimental observations<sup>4-6</sup>. If, however, we inspect the structures (4a)—(10a), we observe that the *quality* of the molecular branching differs. It should be noted that in the isomeric structures studied [*i. e.*: (5a), (6a), (8a), (9a), and (10a); (4a) and (7a)] all the other main

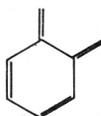


structural factors (the number of atoms and bonds, the type of ring) determining the total  $\pi$ -electronic energy<sup>29</sup> (and thus stability)<sup>30</sup> are identical. It follows, therefore, that the *degree* and the *type* of ring branching may be expected to provide qualitative insight into, and a simple criterion of, the stability of isomeric conjugated systems. This much should also be of help in answering question (iii). Before doing this, however, we mention a few additional details; firstly, a major part of the total  $\pi$ -electronic energy is determined by the number of atoms and bonds contained within a particular molecule<sup>23,29,31</sup>; ring branching (which, however, may have a dominant influence on the molecular stability) makes a relatively small contribution to the energy (<5%)<sup>31</sup>. An important fact to note is that an *even* chain causes only a small perturbation of the ring system<sup>17,23,29,32</sup>, whereas an *odd* chain perturbs ring systems quite considerably.

A classic example is provided by a comparison between styrene (12) and its valence isomer *o*-xylylene (13):



(12)



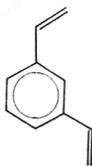
(13)

Styrene is stable, aromatic compound<sup>33</sup> which has been well-characterized<sup>34</sup>, while *o*-xylylene (1,2-benzenequinododimethide) is a very reactive species<sup>35</sup>, which has been characterized only indirectly in the adduct form<sup>36</sup> and in metal complex<sup>37</sup>. Very recently, it has been also described the photochemical preparation of *o*-xylylene in rigid glass<sup>38</sup>. The stability of *o*-xylylene has been discussed by Gleicher, Newkirk, and Arnold<sup>39</sup> using REPE-index of Hess and Schaad<sup>40</sup> and it has been shown to be unstable non-aromatic species (REPE = 0.005  $\beta$ ). The value of REPE index of styrene is considerably larger (0.043  $\beta$ ).

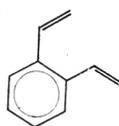
In similar way it could be easily shown how the even chains of different type perturb only slightly a ring system. Compare (14), (15), (16), (17), and (18):



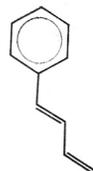
(14)



(15)



(16)



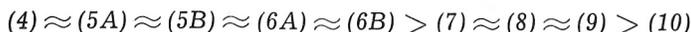
(17)



(18)

whose  $E_\pi$  values ( $E_\pi(14) = 12.86 \beta$ ;  $E_\pi(15) = 12.85 \beta$ ;  $E_\pi(16) = 12.86 \beta$ ;  $E_\pi(17) = 12.93 \beta$ ;  $E_\pi(18) = 12.86 \beta$ )<sup>41</sup> differ insignificantly.

On the basis of the above discussion, the following order of stabilities may be predicted for a sequence of furo- and/or thienoannulated tropylium cations (after inspection of the carbon skeleton of their respective »parent hydrocarbons«):

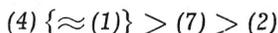


This prediction is actually in accord with experimental evidence, where it is available. We point out that the preparation of (10A) is under way<sup>42</sup>, and it will be of considerable interest to see how well our prediction agrees with subsequent experimental findings.

The presence of various ( $\sigma + \sigma$ )-bivalent heteroatoms may cause minor differences in the stabilities of heterocyclic fused tropylium cations, because it is known that furan and thiophene rings differ in their stabilities<sup>43</sup>. However, the experimental u. v. spectra<sup>42</sup> of (5A), (5B), (6A) and (6B) show only small differences due to a change of a heteroatom.

Finally, we attempt an answer to question (iii). Combining all the rules that have so far been mentioned, we can predict the following order of stabilities:

(a) for mono-annulated tropylium cations



The stabilities of (1) and (4) are expected to be comparable because of the small (second order) perturbation associated with *even* chains, but some differences may occur, as we pointed out, because of the presence of heteroatoms. Unfortunately, the  $pK_R^+$  value of only the thienotropylium cation (4A) is known, and so we can at present only speculate how different the  $pK_R^+$  values of other possible heterocyclic b-side monoannulated tropylium cations (4B) — (4D) might be. If we are willing to accept that the effect of a heteroatom is going to decrease with increase of its size, and the C—X bond length, then going from (4B) through (4A), (4C), to (4D) should bring us closer to (1). It remains to be seen how accurate this prediction will turn out to be in practice.

(b) for di-annulated tropylium cations a similar consideration gives



*Acknowledgements.* — We should like to thank Drs. R. B. Mallion and C. F. Wilcox for helpful comments and help in the presentation of this work. The stay of one of us (N. T.) at the Department of Theoretical Chemistry, University of Oxford was made possible through a grant of Royal Society of London which has been greatly appreciated.

## REFERENCES

1. W. v. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **76** (1954) 3203.
2. H. H. Reinhard, E. Heilbronner, and E. Eschenmoser, *Chem. Ind. (London)* (1955) 415.
3. G. J. Berti, *J. Org. Chem.* **22** (1957) 330.
4. R. G. Turnbo, D. L. Sullivan, and R. Pettit, *J. Amer. Chem. Soc.* **86** (1964) 5630.
5. S. Gronowitz and B. Yom-Tov, *Z. Chem.* **10** (1970) 389.
6. S. Gronowitz, B. Yom-Tov, and U. Michael, *Acta Chem. Scand.* **27** (1973) 2257.
7. M. Stiles and A. J. Libbey, *J. Org. Chem.* **22** (1957) 1243.
8. D. Meuche, W. Simon, and E. Heilbronner, *Helv. Chim. Acta* **41** (1958) 47; *ibid.* **41** (1958) 414.
9. S. Gronowitz, *Arkiv Kemi* **13** (1958) 295.
10. G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta* **43** (1960) 1221.
11. C. W. Bird and G. W. H. Cheeseman, in: *A. Specialist Periodical Report, Aromatic and Heteroaromatic Chemistry*, Vol. 1, The Chemical Society, London 1973, p. 1.
12. A. T. Balaban, *Rev. Roum. Chim.* **15** (1970) 1243; *Tetrahedron* **27** (1972) 6115.
13. H. Hosoya, *Bull. Chem. Soc. Jap.* **44** (1971) 2332; *Theor. Chim. Acta* **25** (1972) 215.
14. A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta* **26** (1972) 67.
15. D. Cvetković, I. Gutman, and N. Trinajstić, *Croat. Chem. Acta* **44** (1972) 365; *Chem. Phys. Lett.* **16** (1972) 614; *J. Chem. Phys.* **61** (1974) 2700; *Theor. Chim. Acta* **34** (1974) 129.
16. I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **20** (1973) 257; *Naturwissenschaften* **60** (1973) 475; *Croat. Chem. Acta* **45** (1973) 423.
17. I. Gutman, N. Trinajstić, and T. Živković, *Tetrahedron* **29** (1973) 3449.
18. I. Gutman, J. V. Knop, and N. Trinajstić, *Z. Naturforsch.* **29b** (1974) 52.
19. M. Randić, *Tetrahedron* **30** (1974) 2067.
20. M. Gordon and T. G. Parker, *Proc. Roy. Soc. (Edinburgh)* **69** (1971) 13.
21. M. Gordon and J. W. Kennedy, *J. C. S. Faraday II* (1973) 484.
22. I. Gutman and N. Trinajstić, *Topics Curr. Chem.* **42** (1973) 49.
23. B. J. McClelland, *J. Chem. Phys.* **54** (1971) 640, I. Gutman, M. Milun, and N. Trinajstić, *ibid.* **59** (1973) 2772.

24. P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.* (1971) 1143.
25. J. V. Knop, N. Trinajstić, I. Gutman, and L. Klasinc, *Naturwissenschaften* **60** (1973) 475.
26. J. V. Knop, N. Trinajstić, and T. Živković, *Coll. Czech. Chem. Commun.* **39** (1974) 2431.
27. N. Trinajstić and T. Živković, to be published.
28. P. L. Watson and R. N. Warrener, *Aust. J. Chem.* **26** (1973) 1725.
29. I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535.
30. L. J. Schaad and B. A. Hess, Jr., *J. Amer. Chem. Soc.* **94** (1972) 3068.
31. I. Gutman, *Chem. Phys. Lett.* **24** (1974) 283; I. Gutman, *Ph. D. Thesis*, University of Zagreb, 1973.
32. I. Gutman, N. Trinajstić, and T. Živković, *Chem. Phys. Lett.* **14** (1972) 342.
33. M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.* **91** (1969) 789.
34. e. g., P. Karrer, *Organic Chemistry*. Elsevier, Amsterdam 1950, p. 402, L. F. Fieser and M. Fieser, *Organic Chemistry*, Reinhold, New York 1956, p. 549.
35. B. Elpern and F. C. Nachod, *J. Amer. Chem. Soc.* **72** (1958) 3379.
36. M. P. Cava and A. A. Deanna, *J. Amer. Chem. Soc.* **81** (1959) 4266.
37. W. R. Roth and J. D. Meier, *Tetrahedron Lett.* (1967) 2053.
38. C. R. Flynn and J. Michl, *J. Amer. Chem. Soc.* **95** (1973) 5802.
39. G. J. Gleicher, D. D. Newkirk, and J. C. Arnold, *J. Amer. Chem. Soc.* **95** (1973) 2526.
40. B. A. Hess, Jr. and L. J. Schaad, *J. Amer. Chem. Soc.* **93** (1971) 305.
41. C. A. Coulson and A. Streitwieser, Jr., *Dictionary of  $\pi$ -Electron Calculation*, Pergamon Press, Oxford 1965.
42. T. Liljefors, U. Michael, B. Yom-Tov, and S. Gronowitz, *Acta Chem. Scand.* **27** (1973) 2485.
43. e. g., N. Trinajstić, *Rec. Chem. Progr.* **32** (1971) 85.

### SAŽETAK

#### Teorija grafova i molekularne orbitale. XIII. O stabilnosti aneliranih tropilijevih kationa

I. Gutman i N. Trinajstić

Primijenjen je topološki pristup za istraživanje podrijetla razlikâ u stabilnosti benzo-aneliranih, te furo- i/ili tieno-aneliranih tropilijevih kationa. Raspoloživi eksperimentalni podaci mogu se tako objasniti, a također se mogu preoreći  $pK_{R^+}$ -vrijednosti za do sada nepoznate spojeve iz toga reda.

INSTITUT »RUDER BOŠKOVIĆ«

41000 ZAGREB

Primljeno 27. svibnja 1974.

ODJEL TEORIJSKE KEMIJE,

SVEUČILIŠTE U OXFORDU

OXFORD OX1 3TG, VEL. BRITANIJA