THEORETICAL STUDY OF ELECTRON STRUCTURE AND STABILITY OF QUASIAROMATIC ANALOGUES OF AZULENE

Pavol ZAHRADNÍK, Elena ĎURČÍKOVÁ and Jaroslav LEŠKA

Department of Organic Chemistry,
Comenius University, 816 31 Bratislava

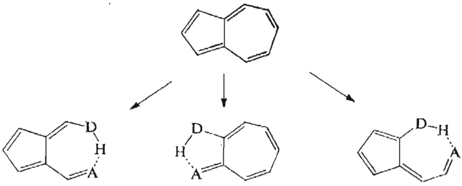
Received November 2nd, 1979

Semiempirical CNDO/2 method was used in the study of 23 quasiaromatic azulene analogues containing a hydrogen bridge A· · H—D, where A and D denote O, NH, or S. The values of the stabilization energy, interaction energy, and changes of Wiberg's indexes suggest that the stability of the studied compounds is caused by a strong hydrogen bond as well as by a strong delocalization of the π-electron system. Derivatives in which A and D are O and NH are especially stable. Derivatives containing an oxo or thioxo group are preferred in tautomeric equilibriums.

There are various experimental and theoretical criterions, according to which organic molecules are classified as aromatic. Some of them are fitted by compounds that are structurally rather different from benzene as an "aromatic standard". If the fragment C—C—C in an aromatic hydrocarbon is formally replaced by an intramolecular hydrogen bridge A···H—D (where A denotes proton acceptor and D proton donor) and the compound preserves its aromatic properties, it is called quasiaromatic[1,2]. Such a system is iso-π-electronic with respect to the original hydrocarbon and the hydrogen bridge is a part of a delocalized π-electron system. Properties typical for aromatic molecules are observed also with their quasiaromatic analogues: owing to delocalization they are extraordinarily stable, they have a planar configuration, the bond lengths are equalized, electrophilic substitutions are possible, *etc.*[1]. Many substances have a quasiaromatic character, *e.g.*, porphyrine derivatives, some terpenoids, *etc.*

Besides experimental findings, the quasiaromatic character was substantiated also by theoretical calculations. For certain quasiaromatic compounds, a theoretical index[3] was calculated by the HMO method, evidencing their stability. Many of them obey the Hückel $4n + 2$ rule extended to polycyclic systems[4]. Based on nonempirical calculations, an assumption was made that the distance of bridge heteroatoms and the presence of a conjugated system are of basic importance for the stabilization of the molecule by an intramolecular hydrogen bond[5]. If the latter is a part of a planar π-electron system, it is much stronger than an analogous intermolecular hydrogen bond[6].

An example of a stable nonbenzenoid aromatic compound is azulene. Several types of quasiaromatic compounds can be formally derived from it (Scheme 1). Most widely known are the derivatives of group *II*, especially the oxygen derivative tropolone. Some of these compounds are both experimentally and theoretically well described[7]. Some compounds of the group *I* were recently prepared and experimentally studied[8]. Formally derived compounds of group *III* have not yet been described.



Group *I* Group *II* Group *III*

SCHEME 1

The object of the present work was to study theoretically the electronic structure, thermodynamic stability, and strength of the hydrogen bond of the quasiaromatic analogues of azulene given in Scheme 1 in dependence on the heteroatoms A and D. We considered derivatives in which A and D were O, NH, and S.

METHOD OF CALCULATION

With respect to the object of our work and character of the studied compounds, we chose the quantum chemical semiempirical CNDO/2 method[9,10], which proved well in studies of systems with a hydrogen bond[11]. Geometric data obtained from X-ray analysis were used if available[12-15]. These were used to obtain a model geometry of compounds for which the experimental data are lacking, or the data from related compounds were used[16]. With sulphur-containing molecules, *d*-orbitals were also involved in the calculations. The stabilization energy was defined as the difference between the total energy of the system without a hydrogen bridge and with it:

In cases where D was oxygen and sulphur, the H atom in the bridge was rotated by 180°, with an NH_2 group by 90° for steric reasons. Nishimoto and coworkers[17] in their study of intramolecular hydrogen bonds analysed the individual biatomic energetical contributions. In our case, the interaction energy between atoms forming the hydrogen bond can be expressed as

$$E^{\mathrm{int}}_{\mathrm{AH}} = E^{\mathrm{res}}_{\mathrm{AH}} + E^{\mathrm{exch}}_{\mathrm{AH}} + E^{\mathrm{coul}}_{\mathrm{AH}}\,. \qquad (1)$$

The first term represents the resonance energy:

$$E^{\mathrm{res}}_{\mathrm{AH}} = 2\beta^0_{\mathrm{AH}} \sum_{\mu} P_{\mu\nu} S_{\mu\nu} \quad \mu \in \mathrm{A},\ \nu \in \mathrm{H} \qquad (2)$$

The second one is the exchange energy:

$$E_{\mathrm{AH}}^{\mathrm{exch}} = -\tfrac{1}{2}\gamma_{\mathrm{AH}} \sum_{\mu} P_{\mu\nu}^2 \quad \mu \in \mathrm{A},\ \nu \in \mathrm{H} \tag{3}$$

and the last one is the Coulombic energy:

$$E_{\mathrm{AH}}^{\mathrm{coul}} = (Z_{\mathrm{A}} - P_{\mathrm{AA}})(Z_{\mathrm{H}} - P_{\mathrm{HH}})\,\gamma_{\mathrm{AH}}\,. \tag{4}$$

The symbols have their usual meaning of the energetic terms of CNDO/2.

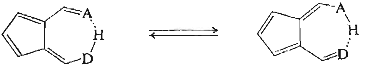
RESULTS AND DISCUSSION

Thermodynamic Stability and Strength of the Hydrogen Bond

The studied systems are summarized in Fig. 1, where the symbols of individual groups correspond to Scheme 1. The relative values of the total energy are also given. It is seen that the compounds with a hydrogen bridge in a five-membered ring (group *II*) are more stable than their isomers with a hydrogen bridge in a seven-membered ring (groups *I* and *III*). This can be attributed to a higher rigidity of group *II* compounds, whereas in the other groups only hydrogen bridge prevents rotation around simple bonds. In accord with expectation, the highest energy corresponds to group *III* compounds, which have an asymmetrical hydrogen bond in a seven-membered ring. Their instability is evidenced also by the fact that they have not been described as yet. Only compound *IIId* has its total energy somewhat lower than the isomer *Id*.

Tautomeric Equilibriums

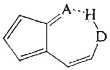
In cases where A and D are different atoms, the following tautomeric equilibriums can be considered with group *I* and *II* compounds:



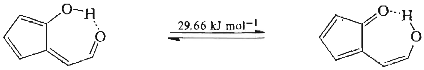
Based on the difference between the total energy of the corresponding tautomers, the energetically preferable tautomeric forms can be predicted. These differences are given in Fig. 1, where the tautomeric pairs are joined with a line. The equilibrium *Ib* ⇌ *Ic* is shifted to the amino-keto form *Ic* in accord with what was found from IR and NMR spectra[8]. A comparatively small energetic difference could, however, make possible the existence of the imino-enol tautomer *Ib*. In the equilibriums *Ia* ⇌ *If* and *Ig* ⇌ *Ih*, the energetic difference is large. Our calculations show uniquely in both cases the preference of the tautomer with a double bond on the S atom, *i.e.*, thioxo-enol form *If* and thioxo-amino form *Ih*.

In group *II*, the equilibrium *IIb* ⇌ *IIc* is shifted to the amino-keto form *IIc* and the equilibrium *IIe* ⇌ *IIf* is shifted to the thioxo-enol form, whose existence was assumed also by Nozoe[18] on the basis of physico-chemical data. Similarly, in the equilibrium *IIg* ⇌ *IIh* the thioxo-amino tautomer *IIh* appears energetically preferable, although the energetic difference is not so marked. The existence of this form is substantiated also by the results of measurement of UV, IR, and NMR spectra[19,20].

Tautomeric equilibriums in group *III* would be related to the existence of another group of azulene analogues:



We studied only the equilibrium



The tautomer with an OH group on the nucleus is somewhat more preferable. The bonding of the heteroatom to the nucleus with a double bond would obviously cause large deformations of the valence angles and thus a lesser energetic stability. We did

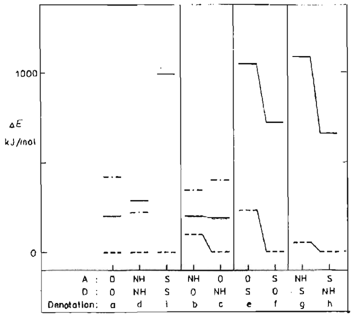


FIG. 1

Relative Total Energies and Tautomeric Equilibriums

——— Group *I*, – – – – group *II*, –.–.– group *III*.

not study other derivatives of this type. Further we shall consider only energetically more preferable tautomers.

An important characteristic of the stability of the studied systems is their stabilization energy (Table I). This is highest with group *I* compounds, which are stabilized by a strong hydrogen bond. The high stabilization energy as compared with values typical for the energy of the hydrogen bond is an evidence that the stabilization energy comprises besides the energy of the hydrogen bond also the delocalization energy due to the formation of a quasiaromatic cyclic system. It is seen that the stabilization energy increases when nitrogen is present in the molecule. Within the individual groups, the highest stabilization energy corresponds to the derivative for which A and D denotes nitrogen. Group *III* is an exception. This value is distored because the model compound without the hydrogen bond has the NH_2 group rotated by 90°, which is energetically less favourable than rotation by 180° in the case of the OH and SH groups. We therefore made comparative calculations where also the OH

TABLE I

Values of Stabilization Energy, Interaction Energy and Dipole Moment

Compound	A	D	Stabil. energy[a]	Interaction energy[a] resonance	exchange	coulomb	$\sum E$	Dip. mom.[b] D
Ia	O	O	89·29	—340·98	—49·17	—91·62	—481·77	2·077 (2·38)[c]
Ic	O	NH	114·76	—205·93	—21·58	—66·03	—293·54	2·747
Id	NH	NH	152·92	—134·53	—13·68	—44·25	—192·46	3·107
If	S	O	46·33	— 60·81	— 4·79	—46·94	—112·54	4·384
Ih	S	NH	91·03	— 9·19	— 0·46	—26·75	— 36·40	6·032
Ii	S	S	17·14	— 6·96	— 0·38	— 6·15	— 13·49	5·648
IIa	O	O	27·59	— 54·42	— 5·33	—51·81	—111·56	4·138 (3·53)[d]
IIc	O	NH	65·41	— 22·57	— 1·52	—37·43	— 61·52	4·193 (3·78)[d]
IId	NH	NH	102·45	— 76·43	— 6·11	—37·04	—119·58	1·950 (1·24)[d]
IIf	S	O	56·11	— 20·15	— 1·32	—37·43	— 58·90	5·804 (4·36)[d]
IIh	S	NH	38·47	— 0·22	— 0·08	—34·95	— 35·25	8·160
IIi	S	S	21·64	— 15·97	— 3·99	— 4·39	— 24·35	6·810
IIIa	O	O	36·76	—168·56	—16·89	—39·22	—224·67	3·749
IIIb	NH	O	43·69	—228·95	—23·98	—30·20	—283·13	5·017
IIIc	O	NH	90·72	— 97·97	— 8·71	—32·90	—139·58	3·534
IIId	NH	NH	89·10	—148·91	—12·96	—25·15	—187·02	0·853

[a] In kJ/mol. [b] Experimental values are given in parentheses (1 D = 3·336 . 10^{-30} C m). [c] Ref.[8]. [d] Ref.[22].

or SH group in the corresponding derivatives were rotated by 90°. Although we obtained higher values for the stabilization energy, the highest one corresponded still to the derivative having nitrogen in place of A and D (ref.[21]). Hence, we can conclude that in the case of 6-amino-1-fulvenecarbimine (*Id*) and 2-amino-2,4,6-cycloheptatrieneimine (*IId*) and extraordinarily stable system is formed owing to delocalization and a strong hydrogen bond. The lowest stabilization energy corresponds to derivatives containing sulphur.

The values of the double-center interaction energy (Table I) defined above give information about the strength of the hydrogen bond in the compounds under study. It is seen that all three its components contribute to the stabilization of the molecules. The interaction energy is high in cases where the proton donor is oxygen or nitrogen. Except for sulphur compounds, the resonance term is a dominant contribution to the interaction energy. Its smallest values are observed in group *II*.

Electron Structure

Considerable changes in the electron structure of molecules take place in forming a hydrogen bridge. Fig. 2 shows the changes in the Wiberg bonding indexes defined as the difference in the Wiberg index of the structure with a hydrogen bond and without it. It is seen that these indexes are larger for single bonds and smaller for double bonds. This is related to leveling the bond lengths during formation of a delocalized system. Although the Wiberg indexes change most markedly near to the heteroatoms A and D, rather large changes occur also in the neighbouring circle, a further evidence that the whole molecule behaves as a delocalized quasiaromatic system. Larger changes take place when A and D are oxygen and nitrogen. In comparing the compounds of groups *I* and *II*, it is seen that larger changes of Wiberg indexes occur in group *I*, again an evidence that the strong hydrogen bond formed causes a relatively strong delocalization of π-electrons. Compounds of group *III* also obey in substance this trend, the changes being smaller on average.

The results of X-ray analysis substantiate the marked delocalization of electrons and the consequent changes in the bond lengths. In group *I*, delocalization causes leveling of the bond lengths, the O atoms in compound *Ia* become equivalent with a C—O bond length[12] of about 0·127 nm, similarly to compound *Id*, where the N atoms are nearly equivalent[15]. With the group *II* compounds, a leveling of the C—N bonds of 2-aminocyclohexaneimine takes place, where the N atoms are equivalent[13], whereas the O atoms in tropolone are not equivalent and also in the seven-numbered ring an alternation of the bonds is observed[7]. Other experimental data, such as the heat of combustion[23] and NMR coupling constants[24] suggest a high stability of tropolone. According to some authors[7], this stability is due more to the strong hydrogen bond than to π-delocalization.

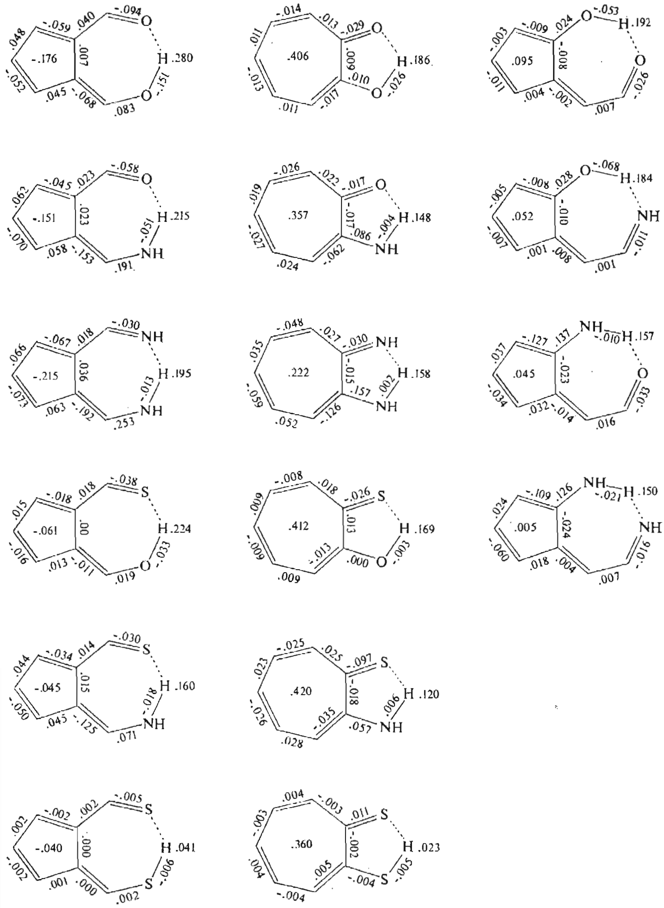


FIG. 2

Changes of Wiberg Bonding Indexes, Charge on Bridge Hydrogen and Total Charge in Carbon Ring

The acidity of the bridge hydrogen can serve also as a criterion of strength of the hydrogen bond. The calculated values of charge on this hydrogen are given in Fig. 2. The compounds of group *I* have more acidic H atom than the analogous compounds of group *II*. Available experimental data also lead to this conclusion: $pK_A = 6{\cdot}92$ for tropolone[25] and $pK_A = 4{\cdot}5$ for 6-hydroxy-1-fulvenecarbaldehyde[8]. The positive charge on the H atom is most influenced by the electronegativity of the proton donor D, less by the electronegativity of the proton acceptor A. In Fig. 2 is shown also the total charge in the carbon ring of the individual derivatives. Compounds of group *I* have a negative charge in the five-membered ring, similarly to the five-membered ring of azulene. The derivative *Id*, where NH stays in place of A and D, has the highest charge. Sulphur-containing compounds have a much smaller charge. For comparison, the negative charge in the five-membered azulene ring is equal to $-0{\cdot}103$. In group *II*, a positive charge is in the seven-numbered ring. Its high values in comparison with azulene $(+0{\cdot}137)$ are due to direct bonding of two electronegative atoms onto the carbon ring. The value of the charge in azulene is best approximated by the derivative in which NH stands for A and D. Compounds of the third group have a positive charge in the five-membered carbon ring, hence also this constant brings no evidence for their aromatic properties.

The dipole moments of the studied compounds are given in Table I. Their calculated values are somewhat higher than the measured ones, except for compound *Ia*. The agreement between them is, however, satisfactory. Dipole moments of group *I* compounds are generally lower than those for the second group. In comparison with the dipole moment of azulene[26] $(\mu_{exp} = 3{\cdot}34 \cdot 10^{-30}\ \text{C. m})$, the values for compounds *Ia*, *Ic*, *Id*, *IId*, and *IIId* are nearest. The low dipole moment of compound *IId* is conspicuous, an evidence for a marked delocalization of π-electrons and equivalence of N-atoms in this system. An extraordinarily low dipole moment was found also for compound *IIId*.

In all the studied systems, the lowest total energy corresponds to cycloheptatriene derivatives of group *II*. Compounds with a thio or oxo group are preferred in tautomeric equilibriums, but imino derivatives are not. Fulvene derivatives of the first group have the highest interaction and stabilization energies, an evidence that the closing of the quasiaromatic cyclic system causes the formation of a strong hydrogen bond and setting free of a considerable delocalization energy. Also the changes of the Wiberg indexes, which are highest in the first group, substantiate the formation of an aromatic system. Group *I* compounds have also the most acidic bridge hydrogen, an evidence for a strong hydrogen bond. The strongest hydrogen bond is formed by oxygen-containing derivatives, whereas the presence of nitrogen makes possible a marked delocalization of π-electrons. The sulphur-containing compounds are much less stabilized, however it should be noted that we used a model geometry in their theory, which could influence the results. The negative charge in the five -membered ring of group *I* compounds and the positive charge in the seven-numbered ring in the group *II* compounds as well as their dipole moments are further evidences for the similarity of these derivatives to their carbon analogue, azulene.

The compounds of the third group are least stable from the point of view of the total energy. The positive charge in the five-membered ring also brings no evidence for the similarity with azulene. The stabilization and interaction energies are smaller than in group *I* but larger than with cycloheptatriene derivatives of group *II*. The derivative *IIId*, where NH stands for A and D, has relativcly the most favourable quantum chemical characteristics.

REFERENCES

1. Lloyd D., Marshall D. R. in the book: *Aromaticity, Pseudoaromaticity, Antiaromaticity.* (E. D. Bergman, B. Pullman, Eds). Israel Academy Sci. Hum., Jerusalem 1971.
2. Kruszewski J., Krygowski T. M.: Bull. Acad. Pol. *23*, 821 (1975).
3. Kruszewski J., Skowroński R.: Soc. Sci. Lodz. Acta Chim. *18*, 70 (1973).
4. Kruszewski J., Krygowski T. M.: Can. J. Chem. *53*, 945 (1975).
5. Isaacson A. D., Morokuma K.: J. Amer. Chem. Soc. *97*, 4453 (1975).
6. Schuster P. in the book: *Hydrogen Bond* (P. Schuster, C. Zundel, C. Sandorfy, Eds). North Holand, New York 1976.
7. Bertelli D. J. in the book: *Topics in Nonbenzenoid Aromatic Chemistry* (T. Nozoe, Ed.), Vol. I. Wiley, New York 1973.
8. Hafner K., Kramer H. E. A., Musso H., Ploss G., Schulz G.: Chem. Ber. *97*, 2066 (1964).
9. Pople J. A., Segal G. A.: J. Chem. Phys. *44*, 3289 (1966).
10. Santry D. P.: J. Amer. Chem. Soc. *90*, 3309 (1968).
11. Dietrich S. W., Jorgensen E. C., Kollman P. A., Rothenberg S.: J. Amer. Chem. Soc. *98*, 8310 (1976).
12. Fuess H., Lindner H. J.: Chem. Ber. *108*, 3096 (1975).
13. Goldstein P., Trueblood K. N.: Acta Crystallogr. *23*, 148 (1967).
14. Shimanouchi H., Sasada Y.: Tetrahedron Lett. *1970*, 2421.
15. Ammon H. L., Mueller-Westerhoff U.: Tetrahedron *30*, 1437 (1974).
16. *Tables of Interatomic Distances and Configuration of Molecules and Ions.* Chem. Soc., London 1958.
17. Ioki Y., Kawana H., Nishimoto K.: Bull. Chem. Soc. Jap. *51*, 963 (1978).
18. Nozoe T., Matsui K.: Bull. Chem. Soc. Jap. *34*, 616 (1961).
19. Nozoe T., Matsui K.: Bull. Chem. Soc. Jap. *34*, 1382 (1961).
20. Brasen W. R., Benson R. E.: J. Amer. Chem. Soc. *83*, 3135 (1961).
21. Ďurčíková E.: *Thesis.* Comenius University, Bratislava 1979.
22. Kurita J.: Sci. Repts. Tohoku Univ. *38*, 85 (1954); Chem. Abstr. *49*, 9989 (1959).
23. Jackson W., Hung T. S., Hopkins H. P.: J. Chem. Thermo. *3*, 347 (1971).
24. Bertelli D. J., Andrews T. G., Crews P. O.: J. Amer. Chem. Soc. *91*, 5286 (1969).
25. Nozoe T. in the book: *Nonbenzenoid Aromatic Compounds* (D. Ginsburg, Ed.). Interscience, New York 1959.
26. Wheland G. W., Mann D. E.: J. Chem. Phys. *17*, 264 (1949).

Translated by K. Micka.