

Structures and Relative Stabilities of Benzenoid and *ortho*-Quinonoid Molecules containing the Divalent Groups $-\text{CH}_2-$, $-\text{NH}-$ and $-\text{O}-$. An *Ab Initio* Study

Anne Skancke and P. N. Skancke

Department of Chemistry, University of Tromsø, P.O. Box 953, N-9001 Tromsø, Norway

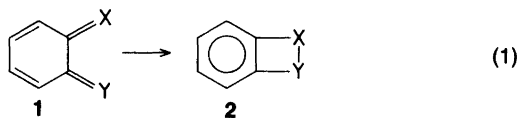
Skancke, A. and Skancke, P. N. 1988. Structures and Relative Stabilities of Benzenoid and *ortho*-Quinonoid Molecules containing the Divalent Groups. $-\text{CH}_2-$, $-\text{NH}-$ and $-\text{O}-$. An *Ab Initio* Study. - Acta Chem. Scand., Ser. A 42: 428-433.

The structures of the ground states of the molecules *o*-quinodimethane (*o*-xylylene) (**1a**), *o*-quinone diimine (**1b**), *o*-benzoquinone (**1c**) and their bicyclic counterparts (**2a-2c**) have been studied by *ab initio* SCF calculations using a split-valence basis. Geometry optimizations have been performed applying analytical gradients. It is confirmed that the open forms have a pronounced single-bond/double-bond alternation in the hexagonal ring, whereas the bicyclic forms have a benzenoid structure. Calculated energies indicate that **2a** is more stable than **1a**. For the other pairs the open, quinonoid forms are found to be energetically preferred. Our predictions are in harmony with available experimental information.

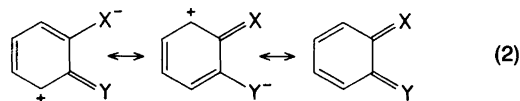
Dedicated to Professor Otto Bastiansen on his 70th birthday

Molecules exhibiting a quinonoid structure constitute a large and important class of organic compounds. A survey of general and theoretical aspects of the chemistry of this class of compounds has recently appeared in the literature.¹

From a structural point of view the *ortho* forms of the quinonoid systems (**1**) pose a particularly interesting problem, owing to a possible conversion to bicyclic benzocyclobutane analogues (**2**) in which the X and Y are different divalent groups such as CH_2 , NH and O .



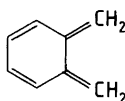
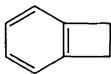
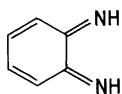
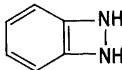
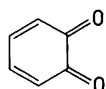
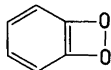
The relative stabilities of the quinonoid forms (**1**) and the bicyclic forms (**2**) are expected to depend strongly on the nature of the substituents. Groups having large electronegativities, such as oxygen, will stabilize the open form (**1**) due to resonance contributions:



Geometrically, the two classes of compounds **1** and **2** are expected to be significantly different. The open, quinonoid forms (**1**) are expected to display a pronounced single-bond/double-bond alternation, whereas the bicyclic forms (**2**) have a more uniform electron density in the ring system, leading to comparatively small differences between bond distances.

The purpose of the present study is to provide a systematic survey of the structural features of the molecular forms **1** and **2**, thereby revealing the structural changes taking place in an interconversion between the forms. Furthermore, we wish to give an estimate of the relative stabilities of the two alternative forms. The dependence of geometries and relative energies on the nature of the groups X and Y is scrutinized by choosing the isoelectronic series CH_2 , NH and O . For computational reasons we have limited the calculations to systems where $X = Y$.

A literature survey of the molecules included in this study is given below.

**1a****2a****1b****2b****1c****2c**

o-benzoquinone (**1c**) is the only stable group 1 molecule at room temperature.²⁻⁴ This compound has been reported to exist in two different forms.³ The red crystalline form has been investigated by X-ray crystallographic techniques,⁴ and it has been revealed that this is the quinonoid form (**1c**).

This molecule has also been studied by microwave spectroscopy in the vapour phase.⁵ The investigation did not lead to a set of structural parameters, but the rotational constants derived from the spectrum were in accordance with the corresponding constants derived from the X-ray study.⁴ This excludes the presence of significant amounts of the valence tautomer **2c** in the vapour phase.

The unsubstituted *o*-quinone diimine **1b** is very unstable and highly reactive.⁶ Accordingly, structural and energetic information on this molecule is not available. However, due to the basic nature of the imine nitrogen, stable salts have been prepared and studied.⁷

The hydrocarbon *o*-quinodimethane (*o*-xylylene) (**1a**) has not been isolated but has been observed in a rigid glass at 77 K following photolysis.⁸⁻¹⁰ It has also been trapped in an argon matrix in the temperature range 8–30 K.¹¹ Furthermore, it has been claimed to occur as an intermediate in a sonochemical reaction in solution at room temperature.¹² No structural data are available for this very unstable species.

The information available on the bicyclic forms appears to be scarce. Only benzocyclobutene (**2a**) has been studied experimentally, in connec-

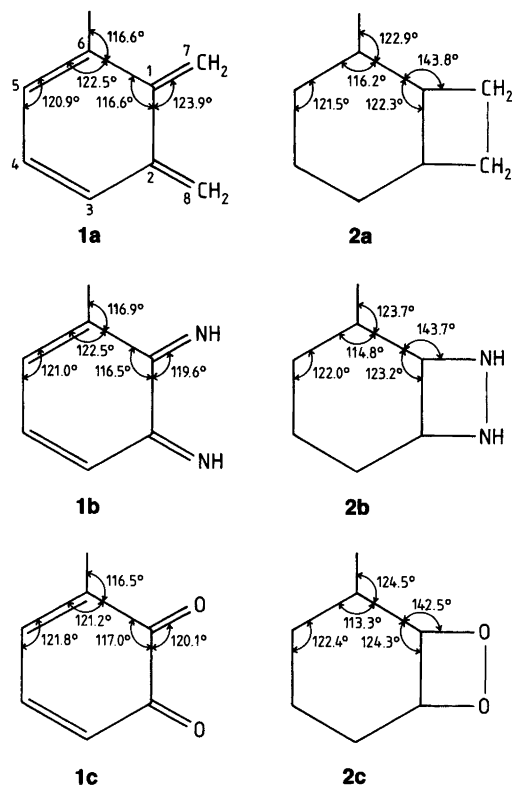


Fig. 1. Valence angles optimized by RHF/3-21G calculations.

tion with measurements on the **1a** \rightleftharpoons **2a** equilibrium.^{13,14} To our knowledge, there is no structural or thermodynamic information available on any of the other bicyclic compounds studied here.

Computations

Geometry optimizations with certain symmetry constraints were undertaken for all the species. The calculations were carried out at the SCF level using analytical gradient techniques as implemented in GAUSSIAN 82.¹⁵ We have chosen the 3-21G basis¹⁶ as a compromise between accuracy and computational costs. It has been shown that a split-valence basis of moderate size is sufficient for reliable predictions of structural differences between related species, although absolute values may be in error.¹⁷

We have assumed closed-shell ground states for all the species. Accordingly, we have used the restricted Hartree-Fock approximation (RHF).

Stability tests¹⁸ of the RHF-solutions indicated that these solutions were internally stable, but unstable relative to UHF-solutions. For **1a**, **1b**, **1c**, **2a** and **2c** assumed to belong to the symmetry group C_{2v} , unrestricted solutions of B_2 symmetry were shown to be preferred. However, the eigenvalues of the second-order instability matrices were found to be very small, viz. -0.07 for the open isomers and -0.02 for the bicyclic molecules. Calculations of $E(^3B_2)$ and $E(^1B_2)$ for **1a** at RHF-optimized geometry confirmed that $E(^1A_1)$ was lowest in this case. We have assumed the same to be valid for the remaining molecules belonging to this symmetry group. The remaining molecule, **2b**, is treated with the assumption of C_s symmetry (the imine H atoms being on the same side of the plane defined by the remaining atoms). For this molecule, the RHF-solution was found to be internally stable but instable relative to UHF-solutions having A'' symmetry. Also in this case, the eigenvalue of the second-order instability matrix was found to be very small, viz. -0.02 . Accordingly, we have also treated this species within the RHF-scheme.

In order to characterize the stationary points obtained by the symmetry-constrained geometry optimizations, vibrational frequencies were calculated analytically at the final geometries using the same basis. For all the molecules except **1a**, only real frequencies were obtained. Thus, the stationary points found for these species are minima.

For **1a** there is one imaginary frequency ($53.9i$ cm^{-1}) belonging to the a_2 representation. This normal mode has as its major deformation a conrotatory twist of the CH_2 groups and some minor displacements of the remaining atoms. The very

low value of the imaginary frequency indicates the presence of a low and broad maximum at the planar form along the a_2 vibrational mode. Consequently, a local minimum of C_2 symmetry is expected to be energetically almost degenerate with the planar form. Therefore we have not pursued a geometry optimization of this species under C_2 symmetry constraint.

Results and discussion

A. Geometries. Complete geometry optimizations were carried out for the molecules **1a–1c** and **2a–2c**. The only constraint introduced during the optimizations was the assumption of planar heavy-atom arrangements in all the molecules. For **1c**, this is at variance with the results of the X-ray investigation indicating a slightly twisted boat conformation of the ring with the oxygen atoms displaced on either side of the mean ring plane.⁴ As this is the only molecule in this series for which experimental structural information is available, a comparison with the experimentally obtained bond distances will serve as an important test of the appropriateness of the calculational level adopted. The data in Table 1 clearly reveal that the predicted bond distances are in harmony with the experimental results. We have confirmed the pronounced single-bond/double-bond alternation in the ring, and we agree with experiment regarding the particularly long $\text{C}_1\text{--C}_2$ bond in the ring, although our predicted value is about 0.025 Å shorter than the measured one. Our predicted double-bond lengths ($\text{C}_3\text{--C}_4$ and $\text{C}=\text{O}$) are also shorter than the observed ones. This may be partly attributed to the basis set, which predicts a $\text{C}=\text{C}$ bond length of 1.315 Å in

Table 1. Predicted bond distances between the heavy atoms (C, N, O) in the molecules **1a–1c** and **2a–2c**. 3–21G basis. Distances in Å. For labelling of atoms see Fig. 1. For **1c**, experimental results are included in parentheses.

Bond	1a	2a	1b	2b	1c	2c
1–2	1.501	1.386	1.506	1.382	1.572(1.552) ^a	1.362
2–3	1.474	1.371	1.477	1.361	1.471(1.469)	1.354
3–4	1.326	1.396	1.324	1.404	1.324(1.341)	1.409
4–5	1.462	1.387	1.464	1.384	1.470(1.454)	1.384
1–7	1.329	1.538	1.261	1.460	1.211(1.220)	1.434
7–8	–	1.599	–	1.537	–	1.521

^aRef. 4.

Table 2. Predicted lengths of the C₁-C₇ bond in **1a-1c** compared with the C=X lengths in the molecules CH₂=XH_n, 3-21G basis. Bond distances in Å.

XH _n	C ₁ -X ₇	C=XH _n
CH ₂	1.329	1.315
NH	1.261	1.256
O	1.211	1.207

ethylene (see Ref. 18 that contains valuable information on this point).

In both **1a** and **1b**, for which no experimental structural information is available, we find the same bonding patterns in the ring, viz. a very long C₁-C₂ bond and two pure double bonds (C₃-C₄ and C₅-C₆). The predicted differences between corresponding ring bond lengths in the series **1a-1c** are too small to justify interpretation.

It is worth noticing that the *exo* double bonds C₁-X₇ are found to have almost the same lengths as in the compounds H₂C=X, thus confirming the dominant single-bond/double-bond alternation characteristic for quinonoid compounds (see Table 2).

To our knowledge, no experimental structural information is available on the valence tautomeric forms **2a-2c**. As shown in Table 1, the predicted bond distances for these molecules indicate that we have a rather uniform electron distribution in the hexagonal ring. Thus, the C₁-C₂ bond varies from 1.386 Å in **2a** to 1.362 Å in **2c**, these distances being significantly longer than that of a pure double bond. Furthermore, the remaining bond distances in the six-membered ring do not deviate much from the "aromatic" C-C distance of 1.40 Å. It is thus fair to conclude that the unsaturated part of the molecules **2a-2c** shows structural features characteristic of aromatic compounds.

A measure of aromaticity may be provided by using different schemes for evaluating aromaticity indices. Several schemes of this kind have been proposed.¹⁹⁻²¹ In our analysis we have adopted the index suggested by Julg:¹⁹

$$A = 1 - \frac{225}{n} \sum_{(rs)} \left[1 - \frac{d_{rs}}{d} \right]^2$$

Table 3. Computed aromaticity indices for the molecules **1a-1c** and **2a-2c**. Structures optimized by 3-21G basis.

Molecule	Index
1a; 2a	0.42; 0.99
1b; 2b	0.38; 0.96
1c; 2c	0.33; 0.93

where d_{rs} is the length of the carbon-carbon ring bond C_r-C_s, d is the weighted mean value of the lengths of all bonds, and the summation extends over all bonds of the ring. The quantity n indicates the number of bonds in the ring.

For benzene, the value of the aromaticity index will be $A = 1$, whereas for the hypothetical molecule cyclohexatriene we have $A = 0$.

The values obtained for the aromaticity index are given in Table 3. These values fall into two distinct groups, one group in the region 0.42 to 0.33 comprising the molecules **1a-1c**, and one group in the region 0.99-0.93 comprising the bicyclic compounds **2a-2c**. These values indicate clearly that the quinonoid molecules have weak aromatic character whereas the bicyclic valence tautomer forms have strong aromatic character. Within each group the variations are rather small. However, it is worth noticing that the pure hydrocarbons, **1a** and **2a**, have a higher aromaticity index than the corresponding hetero-atom compounds. This is in harmony with the general consensus that increased polarity in a molecule reduces its aromatic character.

In all the molecules included in this study the six-membered ring has significant in-plane distortions (see Fig. 1). The angle C₂-C₁-C₆ has values between 116.5 and 117.0° in the quinonoid compounds, whereas the angle C₁-C₆-C₅ has values between 113.3 and 116.2° in the bicyclic forms. Furthermore, the C-H bond adjacent to the *exo*-group in the quinonoid compounds leans towards this group, as indicated by C₁-C₆-H angles in the region 115.5-116.9°.

In Table 4 the C-X bond distances obtained for the bicyclic molecules are compared with the C-X distances in CH₃-XH_n calculated using the same basis. As revealed by the data in the table, these distances in the bicyclic molecules have values typical for an sp³-hybridized carbon atom, in

Table 4. Predicted lengths of the C₁-X₇ bond in **2a-2c** compared with the C-X bond lengths in the molecules CH₃-XH_n, 3-21G basis. Bond distances in Å.

XH _n	C ₁ -X ₇	CH ₃ -XH _n
CH ₃	1.538	1.542
NH ₂	1.460	1.471
OH	1.434	1.441

spite of a trigonal arrangement around the carbon atom at the ring junction.

The X-X bonds are found to be exceptionally long, the C-C bond length having a value of 1.599 Å. These remarkably long bond distances may be attributed to internal strain in the four-membered rings which are related to cyclobutene.

In cyclobutene itself, the single bond facing the double bond is confirmed to be abnormally long, both by experimental and theoretical studies. A microwave investigation has led to a value of 1.566 Å,²² whereas an optimization using the basis set applied here gives the value 1.593 Å.²³ The latter value is virtually the same as that obtained for the corresponding bond in **2a**.

The N-N and O-O bond distances predicted in (**2b**) and (**2c**), viz. 1.537 Å and 1.521 Å, respectively, are also abnormally long by comparison with the corresponding distances of 1.415 Å and 1.473 Å found for N₂H₄ and H₂O₂, respectively.¹⁸

After our calculations were completed, an *ab initio* study including cyclobutene, 1,2-dioxetene and 1,2-diazetene was published.²⁴ Geometry optimizations of these molecules using a 3-21G basis led to C-C, N-N and O-O distances of 1.593 Å, 1.524 Å and 1.502 Å, respectively. These values are very close to the X₇-X₈ distances given in Table 1.

B. Energies and Relative Stabilities. In Table 5 are given the total energies of the open forms **1a-1c** and the relative energies of their valence tautomers **2a-2c**. Energy values obtained at the SCF level using a split-valence basis without polarization functions should be treated with caution. As the bicyclic and open forms represent valence tautomeric pairs where both members have closed shell structures, correlation energy correc-

Table 5. Total energies (in a.u.) and relative energies $\Delta E = E(1) - E(2)$ (in kcal mol⁻¹) obtained by 3-21G calculations at optimized geometries.

-E		ΔE	
1a	305.82312	2a	14.6
1b	337.62034	2b	-23.2
1c	377.08913	2c	-65.9

tions to the predicted energy differences should be small. The lack of polarization functions in the basis will probably favour the open forms, due to strain in their bicyclic counterparts. Thus, the predicted stability of **2** relative to **1** may be somewhat underestimated.

The energetics of the conversion reaction and of the equilibrium for the hydrocarbon pair **1a**, **2a** have been studied experimentally.^{13,14} These experiments have provided values for the activation energies both for the cyclisation reaction **1a** → **2a** and the reverse process. From these data we find an experimental value for the total energy difference, $E(\mathbf{1a}) - E(\mathbf{2a})$, of 10.6 kcal mol⁻¹. This value is in good agreement with our theoretical estimate of 14.6 kcal mol⁻¹, indicating that errors due to the use of a limited basis set and to neglect of electron correlation are cancelled.

For the remaining pairs there is no corresponding experimental information available. Our calculations give the values -23.2 kcal mol⁻¹ and -65.9 kcal mol⁻¹ for the energy differences $E(\mathbf{1b}) - E(\mathbf{2b})$ and $E(\mathbf{1c}) - E(\mathbf{2c})$, respectively. This implies that the open, quinonoid forms are more stable than the bicyclic, benzenoid forms when the hetero-atoms N and O are introduced. This relative energy lowering of the quinonoid forms may be interpreted in terms of a resonance stabilization depicted above [see (2)]. Attempts to relate the energy difference between the two forms to the electronegativities of the *exo*-groups (CH₂, NH, O) have previously been made on the basis of Hückel calculations.²⁵

References

1. Skancke, A. and Skancke, P. N. In: Patai, S. and Rappoport, Z., Eds., *The Chemistry of Quinonoid Compounds*, Wiley, New York 1987, Vol. 1, Chap. 1.

2. Tedder, J. M. and Nechvatal, A. *Basic Organic Chemistry*, Wiley, New York 1967, Part 2.
3. Horspool, W. M. *Quart. Rev.* 23 (1969) 204.
4. Macdonald, A. L. and Trotter, J. *J. Chem. Soc., Perkin Trans. 2* (1973) 476.
5. Blackman, G. L., Brown, R. D. and Porter, A. P. *J. Chem. Soc., Chem. Commun.* (1975) 499.
6. Grundmann, C. In: *Houben-Weyl*, Thieme Verlag 1979, Vol. 7, parts 3a and 3b.
7. Venuvalalingam, P., Singh, U.S., Subbaratnam, N. R. and Kelkar, V. K. *Spectrochim. Acta, Part A* 36 (1980) 103.
8. Migirdicyan, E. *C. R. Hebd. Séances Acad. Sci., Ser. C* 266 (1968) 756.
9. Flynn, C. R. and Michl, J. *J. Am. Chem. Soc.* 95 (1973) 5802.
10. Flynn, C. R. and Michl, J. *J. Am. Chem. Soc.* 96 (1974) 3280.
11. Tseng, K. L. and Michl, J. *J. Am. Chem. Soc.* 99 (1977) 4840.
12. Han, B. H. and Boudjouk, P. *J. Org. Chem.* 47 (1982) 751.
13. Bock, H., Mohmand, S., Hirabayashi, T., Maier, G. and Reisenauer, H. P. *Chem. Ber.* 116 (1983) 273.
14. Roth, W. R. and Scholz, B. P. *Chem. Ber.* 114 (1981) 3741.
15. Binkley, J. S., Frisch, M., Raghavachari, K., DeFrees, D., Schlegel, H. B., Whiteside, R., Fluder, E., Seeger, R. and Pople, J. A. *GAUSSIAN 82, Release A*, Carnegie-Mellon University, Pittsburgh 1985.
16. Binkley, J. S., Pople, J. A. and Hehre, W. J. *J. Am. Chem. Soc.* 102 (1980) 939.
17. Hehre, W. J., Radom, L., von Rague Schleyer, P. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York 1986.
18. Seeger, R. and Pople, J. A. *J. Chem. Phys.* 66 (1977) 3045.
19. Julg, A. and Francois, Ph. *Theor. Chim. Acta* 7 (1967) 249.
20. Kruszewski, J. *Societatis Scientiarum Lodziensis, Acta Chim. Lodz.* 16 (1971) 77.
21. Polansky, O. E. and Derflinger, G. *Int. J. Quant. Chem.* 1 (1967) 249.
22. Bak, B., Led, J. J., Nygaard, L., Rastrup-Andersen, J. and Sørensen, G. O. *J. Mol. Struct.* 3 (1969) 369.
23. Rondau, N. G. and Houk, K. N. *J. Am. Chem. Soc.* 107 (1985) 2099.
24. Budzelaar, P. H. M., Cremer, D., Wallasch, M., Würthwein, E.-U. and Schleyer, P. v. R. *J. Am. Chem. Soc.* 109 (1987) 6290.
25. Kolshorn, H. and Meier, H. *Z. Naturforsch., A* 32 (1977) 780.

Received January 25, 1988.