

AM1 STUDY OF SINGLE-ATOM *PERI*-BRIDGED NAPHTHALENES

ISSA YAVARI*

Chemistry Department, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran

AND

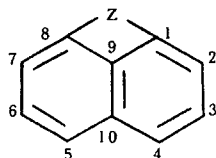
DAVOOD NORI-SHARGH

Chemistry Department, Islamic Azad University, P.O. Box 19395-1775, Tehran, Iran

peri-Bridged naphthalenes in which the C-1 and C-8 atoms of the naphthalene ring are bonded to a single atom in a bridging group Z ($Z = \text{CH}_2, \text{CHBr}, \text{C}=\text{O}, \text{NH}, \text{O}, \text{S}, \text{S}=\text{O}$ and SO_2) were studied by the AM1 semi-empirical SCF MO method. Although in *peri*-naphthalenes bridged by carbon or sulfur the naphthalene structure is planar, the corresponding nitrogen- or oxygen-bridged molecules are distorted about 15 and 23°, respectively. There are significant variations (from 92 to 106°) of the C-1-C-9-C-8 angle that is calculated in the cycle formed by the bridge. The calculated strain-energy barrier for pyramidal atom inversion in amine 4 and sulfoxide 7 are 32.5 and 174 kJ mol⁻¹, respectively.

INTRODUCTION

Single-atom *peri*-bridged naphthalene compounds containing a four-membered carbocyclic or heterocyclic ring have two special torsional constraints and have interesting structural features.¹⁻⁴ In these molecules the C-1 and C-8 atoms are bonded to a single atom in a bridging group Z. The presence of the four-membered ring imposes steric and electronic effects on the naphthalene system. Compounds of this type are therefore of interest.



- | | |
|------------------------|------------------------|
| 1, Z = CH ₂ | 5, Z = O |
| 2, Z = CHBr | 6, Z = S |
| 3, Z = C=O | 7, Z = SO |
| 4, Z = NH | 8, Z = SO ₂ |

There are as yet few examples in which the *peri* positions of naphthalene have been bridged by one atom. The first report on a *peri*-bridged naphthalene was the synthesis of naphtho[1,8-*bc*]thiethene 1,1-dioxide (8) in 1965.³ Bailey and Schechter⁴ succeeded in preparing the carbon-bridged parent hydrocarbon (1) in 1974.

* Author for correspondence.

Despite the successful synthesis of *peri*-naphthalenes bridged by sulfur or carbon, the corresponding nitrogen- or oxygen-bridged molecules are not known.⁵ We report here Austin Model 1 (AM1)⁶ semi-empirical SCF MO calculations for compounds 1-8. This computational method provides especially reliable results for various structural aspects of organic molecules.

CALCULATIONS

Semi-empirical calculations were carried out using the AM1 method with the MOPAC 6.0 program^{7,8} implemented on a VAX 4000-300 computer. Energy-minimum geometries were located by minimizing energy, with respect to all geometrical coordinates, and without imposing any symmetry constraints. The structures of the transition-state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*⁹ (Keyword SADDLE). All structures were characterized as stationary points, and true local energy minima and energy maxima on the potential energy surface were found using the Keyword FORCE. All energy-minima and energy-maxima geometries obtained in this work are calculated to have $3N-6$ and $3N-7$ real vibrational frequencies, respectively.¹⁰

RESULTS AND DISCUSSION

Representative structural parameters for *peri*-bridged naphthalenes 1–8, as calculated by the AM1 method, are given in Table 1. X-ray structures have been obtained on naphthalene¹² and two *peri*-fused naphthalenes 2¹³ and 8.¹⁴ The agreement between the calculated and the experimental structures is fairly good. The most striking features of these molecules are the changes in bonding parameters in the naphthalene moiety on being *peri*-bridged. The bonds to the Z bridge, which might be expected to be unusually stretched, are only about 0.04 Å longer than a C–C or C–X (X = O, N, S) single bond, and their lengths are similar to those in planar four-membered rings.² Distortions in a molecule are rarely concentrated in one degree of freedom. The general reason for this is that the energy of the distortion is approximately quadratically dependent on the size of the distortion. The sum of the squares of several small numbers is always much

smaller than the square of the sums, so there will be a number of small distortions rather than a large one. Therefore, the strain due to the bridging of the *peri*-positions is not concentrated solely in the Z–C-1 and Z–C-8 bridge bonds, but rather is expressed by adjustments, particularly in bond angles, throughout the molecules. This feature may account for the unexpected thermal stability of some of these systems.

The interatomic distance between the C-1 and C-8 positions in naphthalene is calculated by AM1 to be 2.28 Å. The net effect of bridging the *peri*-positions has been to compress that portion of the naphthalene nucleus directly connected to the bridge and to cause the opposite side of the molecule to expand. The ratio (*R*) of C-4–C-5 to C-1–C-8 interatomic distances in the *peri*-bridged systems 1–8 may be considered as a criterion for their stabilities. For *R* greater than *ca* 1.3, as in 4 and 5, the *peri*-bridged system is highly strained. Compounds 1–3, with *R* values of about 1.25, are fairly stable. The bridged sulfide 6 and its oxides 7 and

Table 1. Calculated structural parameters^a and energies in compounds 1–8

Parameter	Naphthalene <i>D</i> _{2h}	1, Z = CH ₂ <i>C</i> _{2v}	2, Z = CHBr <i>C</i> _s	3, Z = CO <i>C</i> _{2v}	4, Z = NH <i>C</i> _s <i>C</i> _{2v}	5, Z = O <i>C</i> _s	6, Z = S <i>C</i> _{2v}	7, Z = SO <i>C</i> _s <i>C</i> _{2v}	8, Z = SO ₂ <i>C</i> _{2v}
Bond length (Å)									
C-1–Z	— (—)	1.55	1.55 (1.57)	1.54	1.48 1.43	1.46	1.79	1.81 1.78	1.76 (1.82)
C-1–C-2	1.37 (1.36)	1.36	1.36 (1.36)	1.36	1.36 1.37	1.36	1.36	1.36 1.37	1.36 (1.37)
C-1–C-9	1.42 (1.44)	1.43	1.43 (1.37)	1.43	1.43 1.43	1.42	1.43	1.43 1.44	1.43 (1.40)
C-2–C-3	1.42 (1.42)	1.44	1.44 (1.43)	1.44	1.44 1.45	1.45	1.44	1.43 1.43	1.43 (1.43)
C-3–C-4	1.37 (1.36)	1.38	1.38 (1.38)	1.38	1.39 1.39	1.39	1.38	1.38 1.38	1.38 (1.38)
C-4–C-10	1.42 (1.43)	1.43	1.43 (1.42)	1.43	1.44 1.44	1.44	1.44	1.43 1.43	1.43 (1.44)
C-9–C-10	1.42 (1.41)	1.37	1.37 (1.38)	1.38	1.37 1.37	1.37	1.38	1.39 1.39	1.38 (1.38)
Bond angles (°)									
Z–C-1–C-9	— (—)	88	88 (89)	87	90 88	91	90	89 87	89 (—)
C-1–Z–C-8	— (—)	87	87 (83)	89	88 92	87	78	77 80	79 (74.5)
C-1–C-2–C-3	120 (120)	116	116 (115)	116	115 115	114	117	118 118	118 (—)
C-1–C-9–C-10	119 (119)	132	132 (131)	131	132 132	131	128	128 127	129 (—)
C-1–C-9–C-8	122 (122)	97	97 (99)	97	92 92	90	103	104 106	103 (106)
C-2–C-1–C-9	120 (120)	116	116 (118)	116	116 116	117	117	117 116	116 (—)
C-2–C-3–C-4	— (—)	126	126 (125)	126	126 127	127	124	124 124	124 (—)
C-3–C-4–C-10	— (—)	120	120 (121)	120	120 119	119	120	120 120	120 (—)
C-4–C-10–C-5	— (—)	137	138 (138)	137	139 139	139	133	132 131	133 (133)
C-4–C-10–C-9	— (—)	112	111 (110)	111	110 110	110	114	114 114	114 (—)
Torsion angle (°)									
C-1–C-9–C-10–C-5	180 (180)	179	179 (180)	180	164 165	157	180	179 177	180 (180)
Non-bonded distance (Å)									
C-1–C-8	2.48 (2.48)	2.14	2.13 (2.08)	2.15	2.08 2.06	2.02	2.24	2.25 2.29	2.23 (2.22)
C-4–C-5	2.48 (2.48)	2.66	2.67 (2.69)	2.66	2.69 2.70	2.69	2.62	2.61 2.60	2.60 (2.61)
Energy									
ΔH_f° ^b	— (—)	478.9	508.1 (—)	391.4	598.9 631.4	513.7	430.4	278.7 452.7	149.6 (—)
ΔH_s° ^c	— (—)	—	— (—)	—	0.0 32.5	—	—	0.0 174.0	— (—)

^aExperimental values are given in parentheses.

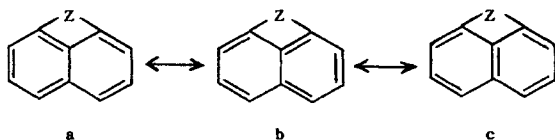
^bHeats of formation in kJ mol⁻¹.

^cThe standard strain energy in each geometry of a molecule is defined as the difference between the standard heats of formation (ΔH_f°) for the geometry and the most stable conformation of the molecule.¹¹

8, with R values of less than 1.2, are more stable than their carbocyclic analogues 1–3.

The force constants for bending angles are much smaller than those for stretching bonds. Thus it is noteworthy that some of the internal angles in the naphthalene moiety of compounds 1–8 are compressed to a minimum of 109° or expanded to 134° . The C-1–C-9–C-8 angle of the four-membered ring is compressed to 97° in 1–3, to about 92° in 4 and 5 and to 103° in 6–8. The C-4–C-10–C-5 angle, on the other side of the naphthalene moiety in 1–8, is expanded to 132 – 142° .

The variation in the C–C bond distances in the naphthalene rings in 1–8 is most easily accounted for on the basis that the contribution of the symmetrical Kekulé structure **c** to the resonance hybrid of these compounds is in fact more important than those of **a** and **b**. This is in agreement with Clar's rule¹⁵ on the relative importance of individual Kekulé structures, which states that the preferred resonance structures are those which maximize the number of isolated aromatic sextets.¹⁶



Compounds 4 and 7 can undergo pyramidal atom inversion. The calculated strain-energy barrier for nitrogen inversion in amine 4 is 32.5 kJ mol^{-1} , which is close to that observed in simple azetidines.¹⁷ Inversion of the sulfoxide 7 requires about 174 kJ mol^{-1} , which is consistent with the chiral stabilities of the sulfoxides.¹⁸

As shown in Table 1, the C-1–C-9–C-10–C-5 torsion could be regarded as a measure of non-planarity of the *peri*-bridged naphthalenes 1–8. The naphthalene structure of *peri*-naphthalenes bridged by carbon (1–3) or sulfur (6–8) is essentially planar with the C-1–C-9–C-10–C-5 torsional angle being about 0 – 1° . Thus, buckling of these molecules is only barely significant. However, the corresponding nitrogen- or oxygen-bridged molecules are fairly distorted by about 15 – 23° , respectively. The Z–C-1 and Z–C-8 bonds in these

molecules are considerably shorter than those in carbon- or sulfur-bridged systems.

In conclusion, it can be said that in naphthalenes which are bridged in the *peri*-position by one atom, the imposed strain is reflected by changes in the bond angles and, to some extent, by changes in bond lengths, rather than deformation of the aromatic nucleus. The stabilizing effect of the planar π -system makes the formation and existence of extremely strained molecules such as 1, 2, 6, 7 and 8 possible.

REFERENCES

1. F. Vogtle, *Fascinating Molecules in Organic Chemistry*. Wiley, New York (1992).
2. E. Block, in *Comprehensive Heterocyclic Chemistry*, edited by A. R. Katritzky and C. W. Rees, Vol. 7, Chapt. 5, pp. 403–447. Pergamon Press, Oxford.
3. R. W. Hoffmann and W. Sieber, *Angew. Chem., Int. Ed. Engl.* **4**, 876 (1965); *Justus Liebigs Ann. Chem.* **730**, 96 (1967).
4. R. J. Bailey and H. Schechter, *J. Am. Chem. Soc.* **96**, 8116 (1974).
5. A. J. Gordon, *J. Org. Chem.* **35**, 4261 (1970); D. C. De Jongh and G. N. Evenson, *J. Org. Chem.* **37**, 2152 (1972).
6. M. J. S. Dewar, E. G. Zeobisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985); M. J. S. Dewar and K. M. Dieter, *J. Am. Chem. Soc.* **108**, 8075 (1986).
7. J. J. P. Stewart, *QCPE 581*. Department of Chemistry, Indiana University, Bloomington, IN.
8. J. J. P. Stewart, *J. Comput.-Aided Mol. Des.* **4**, 1 (1990).
9. M. J. S. Dewar, E. F. Healy and J. J. P. Stewart, *J. Chem. Soc., Faraday Trans. 2* **80**, 227 (1984).
10. J. W. McIlver, Jr, *Acc. Chem. Res.* **7**, 72 (1974).
11. E. M. Arnett, J. C. Sanda, J. M. Bollinger and M. Barber, *J. Am. Chem. Soc.* **89**, 5389 (1967).
12. D. W. J. Cruickshank, *Acta Crystallogr.* **10**, 504 (1957).
13. M. Gessner, P. Card, H. Schechter and G. G. Christoph, *J. Am. Chem. Soc.* **99**, 237 (1977).
14. J. Meinwald, S. Knapp, S. K. Obendorf and R. E. Hughes, *J. Am. Chem. Soc.* **98**, 664 (1976).
15. E. Clar, *The Aromatic Sextet*. Wiley, New York (1972).
16. A. Moyano and J.-C. Paniagua, *J. Org. Chem.* **56**, 1858 (1991).
17. J.-M. Lehn, *Fortschr. Chem. Forsch.* **15**, 311 (1970).
18. K. K. Anderson, in *The Chemistry of Sulphones and Sulfoxides*, edited by S. Patai, Z. Rappoport and C. Stirling, pp. 55–94. Wiley, Chichester (1988).