

An ab initio study of annulation effects on the valence isomerism of benzene

Alan B. Brown^{a,*}, Scott E. McKay^a, Paul Kiprof^b

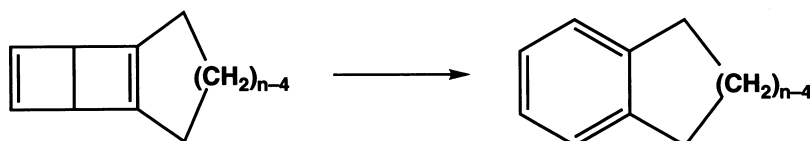
^aDepartment of Chemistry, Florida Institute of Technology, Melbourne, FL 32901, USA

^bDepartment of Chemistry, University of Minnesota Duluth, Duluth, MN 55812, USA

Received 1 November 1996; accepted 20 February 1997

Abstract

Annulation should tilt the benzene/Dewar-benzene equilibrium toward benzenes the largest effective annulating ring being six-membered; MP2(fc)/6-31G**/RHF/6-31G* methods are needed to reproduce experimental isomerization energies, but 6-31G calculations suffice to show trends for molecular design.



Smaller “*n*” should favor isomerization; effective rings will have $n \leq 6$.

© 1997 Elsevier Science B.V.

Keywords: Annulation; Valence isomerism; Benzene

1. Introduction

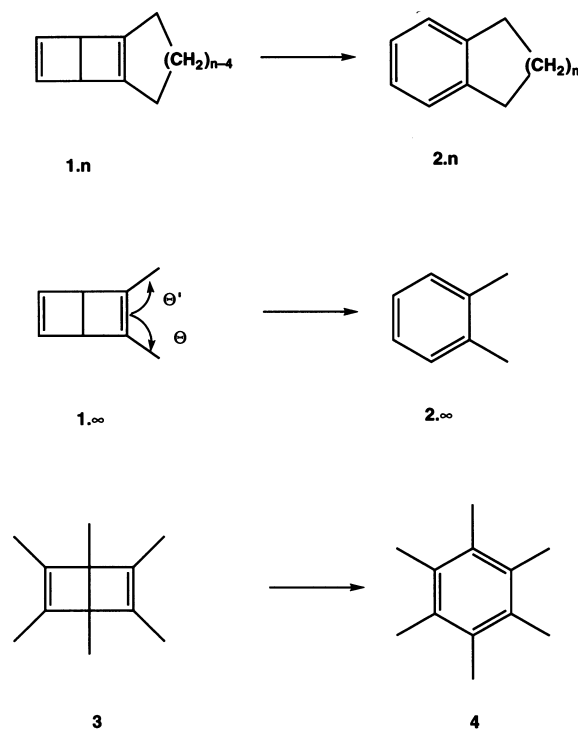
Benzene valence isomerism is known to depend on substitution [1]; for example, the first synthesis of a Dewar benzene depended on destabilization of a benzene by juxtaposition of bulky substituents [2]. Annulated benzenes are the subject of current interest, in connection with attempts to induce bond-length alternation [3]. For the past several years, as part of an effort to produce an isolable [5]paracyclophane [4], we have been studying annulation effects on the

equilibrium between benzene and Dewar benzene. By ab initio calculations, we have now compared the energies and geometries of the [*n*]annulated Dewar benzenes **1.n** with those of the corresponding annulated benzenes **2.n** (Scheme 1).

2. Methods

Calculations employed the SPARTAN package, versions 3.0 [5]a and 3.1 [5]b, on a Silicon Graphics Indy platform; default computational parameters were used throughout. Symmetry constraints were *not* used

* Corresponding author.



at any level. Structures were fully optimized by using the AM1 [6] and MNDO [7] semiempirical methods, and by restricted Hartree–Fock ab initio calculations with the STO-3G, 6-31G, and 6-31G* basis sets; single-point MP2(fc)/6-31G*/RHF/6-31G* energies (hereafter termed “MP2”) were calculated [8]. Hexamethyl Dewar benzene (**3**) and hexamethylbenzene (**4**) were also studied, because theirs is the most

Table 1
Isomerization energies (kcal mol⁻¹)

Reaction	ΔE_{6-31G}	ΔE_{6-31G^*}	$\Delta E_{\text{“MP2”}}$
3 → 4	-70.0	-56.8	-58.4 ^a
1.∞ → 2.∞	-93.0	-79.0 ^b	-75.6 ^c
1.8 → 2.8	-94.8	-80.9	-78.8
1.7 → 2.7	-94.0	-79.9	-77.1
1.6 → 2.6	-97.5	-83.3	-79.5
1.5 → 1.5	-111.3	-96.3	-91.4
1.4 → 2.4	-128.8	-112.5	-105.9

^a Exp.: -59.4 ± 2.1 kcal mol⁻¹ [9].

^b RHF/6-311G**.: -78.5 kcal mol⁻¹.

^c MP2(fc)/6-311G**//RHF/6-311G**.: -74.2 kcal mol⁻¹.

closely related isomerization whose experimental ΔH value has been measured [9]; the “MP2” energy difference (isomerization energy) is within the range of the experimental values [9], and the RHF/6-31G* value is almost as good (Table 1). The isomerization energy of the simple system **1.∞** → **2.∞** was calculated by the RHF/6-311G** and MP2(fc)/6-311G**//RHF/6-311G** methods; these values were within 1.4 kcal mol⁻¹ of the RHF/6-31G* and “MP2” values respectively. This suggests that the agreement between the “MP2” and experimental values for **3** → **4** represents a real convergence of theory with experiment, not happenstance.

3. Results and discussion

The calculated isomerization energies for **1.n**–**2.n** (Table 1) are similar for $n = \infty$ and $n = 7$; the “no-ring” models are 2,3-dimethyl Dewar benzene (**1.∞**) and *o*-xylene (**2.∞**), because the Dewar and benzene fragments of **1.n** and **2.n** ($n \neq \infty$) bear carbon substituents in the same places as the methyls of **1.∞** and **2.∞**. Isomerization becomes more exothermic for $n < 6$ than for no ring; the “threshold” ring (the largest with any significant effect) is six-membered. Progressively larger jumps in exothermicity are predicted from $n = 6$ to $n = 5$ and from $n = 5$ to $n = 4$. The trend reflects an annulation effect, not merely ring strain: the strain of simple cycloalkenes *decreases* from seven to six members [10].

The level of theory needed in these systems depends on the purpose of the calculations. Bonding in Dewar benzenes is difficult to describe using hybrids of *s* and *p* Gaussian functions only [11]; *for quantum chemistry*, therefore, it seems evident that carbon *d* polarization functions and correlation corrections are needed. However, the qualitative finding of a six-membered threshold ring also holds at the 6-31G level (Fig. 1), and 6-31G bond lengths and angles are within 0.02 Å and 0.6° of experimental data where available. Like others, we find that bond alternation is small in benzene rings fused to a single, saturated ring of four or more members [12]. We conclude that, *for molecular design*, in the ring-size range $n = 4$ to $n = 7$, the 6-31G basis set suffices. For $n = 8$, the isomerization energy is close to that for $n = 6$ at the “MP2” level only.

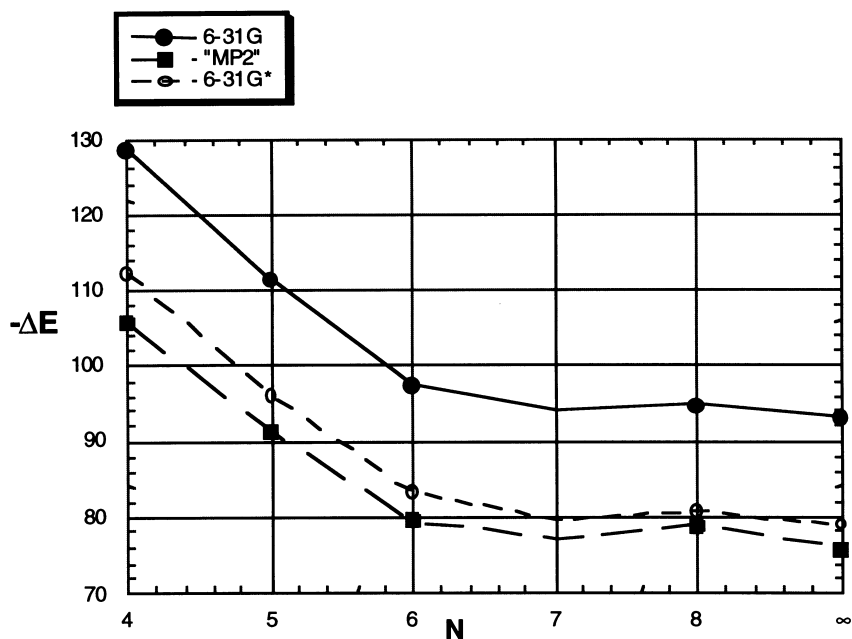


Fig. 1. Isomerization energies (kcal mol⁻¹) versus annulating ring size (*n*).

$$SE_{\text{tot}} = TE_{\text{strained}} - TE_{\text{unstrained}} \quad (1)$$

$$SE_{\text{tot}} = SE_{\text{“bnz”}} + SE_{\text{ann}} \quad (2)$$

$$SE_{\text{“bnz”}} = TE_{\text{“bnz”, def.}} - TE_{\text{benzene}} \quad (3)$$

$$SE_{\text{ann}} = TE_{\text{ann, def.}} - TE_{\text{ann}} \quad (4)$$

The structural basis of the annulation effect was studied by dissection of strain energies [Eqs. (1)–(4)] [13]. The strain energy SE_{tot} is defined as the difference between the total energies of the strained molecule and a fictitious unstrained molecule [Eq. (1)]. One can partition SE_{tot} into two theoretically accessible parts [Eq. (2)] [13]: $SE_{\text{“bnz”}}$ is the difference

between the total energy of the deformed “benzene” (“benzene” in quotes denotes “either benzene or Dewar benzene as appropriate”) and that of benzene itself [Eq. (3)]. Similarly, SE_{ann} is the difference between the total energy of the deformed annulating ring and that of the fully optimized alkane with the same number of sp^3 carbons as the annulating ring [13], e.g., ethane for **2.4** [Eq. (4) and Table 2].

The increase in isomerization exothermicity between **n.7** and **n.6** is reflected in the strain-energy change, and is split about evenly between $\Delta SE_{\text{“bnz”}}$ and ΔSE_{ann} (Table 3). The change in $\Delta SE_{\text{“bnz”}}$ is an *increase* in $SE_{\text{“bnz”}}$ from Dewar benzene **1.7** to **1.6**, but *not* observed going from benzene **2.7** to **2.6**. This effect appears to depend primarily on the “exocyclic”

Table 2

Partial strain energies (in kcal mol⁻¹) [MP2(fc)/6-31G*/RHF/6-31G*]

Cpd	$SE_{\text{“bnz”}}$	SE_{ann}	Cpd	$SE_{\text{“bnz”}}$	SE_{ann}
1.∞	80.91	2.55	2.∞	0.09	5.54
1.8	81.09	8.78	2.8	0.30	10.76
1.7	80.92	5.11	2.7	0.16	6.72
1.6	83.010	4.28	2.6	0.14	3.69
1.5	96.011	13.77	2.5	4.06	10.56
1.4	142.20	38.86	2.4	36.05	33.84

Table 3

Strain energy changes (in kcal mol⁻¹) and “exocyclic” angles (in °) [MP2(fc)/6-31G*/RHF/6-31G*]

Reaction	$\Delta SE^a_{\text{“bnz”}}$	ΔSE^a_{ann}	ΔSE^b_{tot}	ΔSE_{homo}	$\Delta E^c_{\text{“MP2”}}$	Θ^d_{dew}	Θ^e_{ben}
1.∞ → 2.∞	-80.8	+3.0	-77.8		-75.6	135.2	120.9
1.8 → 2.8	-80.8	+2.0	-78.8	-84.8	-78.8	136.5	122.4
1.7 → 2.7	-80.8	+1.6	-79.2	-77.1	-77.1	134.7	121.6
1.6 → 2.6	-83.0	-0.6	-83.6	-79.5	-79.5	126.4	121.6
1.5 → 2.5	-92.1	-3.2	-95.3	-91.4	-91.4	114.1	110.6
1.4 → 2.4	-106.1	-5.0	-111.2	-105.9	-105.9	95.4	93.6

^a ΔSE is the change in SE from **1.n** to **2.n**.^b Sum of previous two columns.^c From Table 1.^d Θ_{av} for **1.n**.^e Θ_{av} for **2.n**.

angles Θ' and Θ (Fig. 1; mean: Θ_{av}), which drop by 8° between **1.7** and **1.6**, but are unchanged between **2.7** and **2.6** (Table 3). Plots of ΔE versus Θ_{av} in the Dewar benzenes are linear (Fig. 2) with $r \geq 0.983$. Thus, annulation affects benzene valence isomerism in large part by manipulating Θ_{av} . Changes in strain energy evaluated in this way (ΔS_{tot}) are close both to strain energy changes evaluated using homodesmotic reactions (ΔSE_{homo}) [13] and to “MP2” energy changes ($\Delta E_{\text{“MP2”}}$; Table 3).

The change in ΔSE_{ann} arises because SE_{ann} does drop significantly from benzene **2.7** to **2.6**, but not from Dewar benzene **1.7** to **1.6**. The effect appears

to come from elongation and narrowing of the six-membered ring of **1.6**, and will be discussed in detail elsewhere.

In sum, benzene valence isomerism can be manipulated by annulation; isomerization of 2,3-annulated Dewar benzenes to annulated benzenes is calculated to become more exothermic with decreasing size of the annulating ring. The largest effective annulating rings are six-membered; the exocyclic C=C–C angles of the Dewar benzene are forced down, and the six-membered ring is deformed. To reproduce experimental isomerization energies, MP2(fc)/6-31G*/RHF/6-31G* methods are needed; for molecular design,

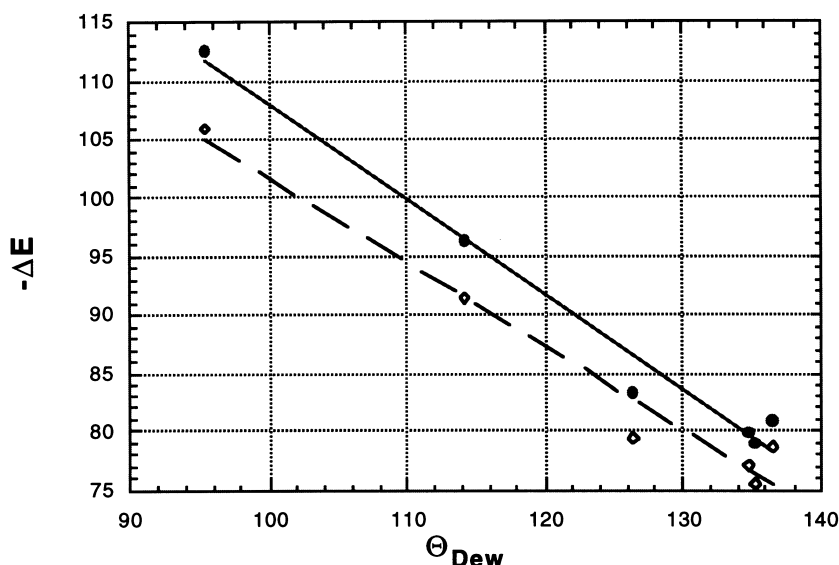


Fig. 2. Isomerization energies (kcal mol⁻¹) versus Θ_{dew} (°), with least-squares lines. ●, 6-31G*, $r = 0.990$; ◇, “MP2”, $r = 0.983$.

6-31G calculations suffice to produce the same trends seen at higher theoretical levels.

Acknowledgements

We are indebted to Professor J. Clayton Baum for many helpful discussions; we thank I. Beros and J.P.M. Fessenden for preliminary calculations, and a referee for several useful suggestions. This study was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society; purchase of computers was assisted by the National Science Foundation.

References

- [1] Review: A.T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-Derivatives, and their Valence Isomers*, Vol. II, CRC, Boca Raton, FL, 1987, pp. 5–21.
- [2] E.E. van Tamelen, S.P. Pappas, *J. Am. Chem. Soc.* 84 (1962) 3789.
- [3] A review of the Mills–Nixon effect: N.L. Frank, J.S. Siegel, *Adv. Theor. Interesting Mol.*, 3 (1995) 209. A very recent overview: A.M. Rouhi, *Chem. Eng. News*, 74(14) (1996) 27.
- See also: F. Cardullo, D. Giuffrida, F.H. Kohnke, F.M. Raymo, J.F. Stoddart, D.H. Williams, *Angew. Chem., Int. Ed. Engl.*, 35 (1996) 339.
- [4] A recent review: F. Bickelhaupt, F.H. de Wolf, *Adv. Strain Org. Chem.*, 3 (1993) 185. The most recent approach: D.S. van Es, F.J.J. de Kanter, W.H. de Wolf, F. Bickelhaupt, *Angew. Chem., Int. Ed. Engl.*, 34 (1995) 2553.
- [5] *Spartan Users Guide*, Versions (a) 3.0 and (b) 3.1, Wavefunction, Inc., Irvine, CA, (a) 1993 and (b) 1994.
- [6] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J. Am. Chem. Soc.*, 107 (1985) 3902; 115 (1993) 5348.
- [7] M.J.S. Dewar, W. Thiel, *J. Am. Chem. Soc.* 99 (1977) 4899.
- [8] For methods, see W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986, pp. 10–42, 63–100.
- [9] W. Schäfer, *Angew. Chem., Int. Ed. Engl.* 5 (1966) 669; J.F.M. Oth, *Recl. Trav. Chim. Pays-Bas*, 87 (1968) 1185; W. Adam, J.C. Chang, *Int. J. Chem. Kinet.*, 1 (1969) 487.
- [10] S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E. O’Neal, A.S. Rodgers, R. Shaw, R. Walsh, *Chem. Rev.*, 69 (1969) 279 and references therein.
- [11] An early discussion: M. Randic, Z. Majerski, *J. Chem. Soc. B*, (1968) 1289.
- [12] A recent example with leading references: A. Stanger, N. Ashkenazi, A. Schachter, D. Blaser, P. Stellberg, R. Boese, *J. Org. Chem.* 61 (1996) 2549.
- [13] F. Bockisch, J.C. Rayez, D. Liotard, B. Duguay, *J. Comput. Chem.* 13 (1992) 1047.