bond angle of $[HAlN(i\text{-}Pr)]_4$[29] and $[MeAlN(i\text{-}Pr)]_4$[29] tends to be slightly smaller than the N–Al–N bond angle, has been noted previously. This trend was followed by other cage compounds that were studied.[31,41] However, in $(PhAlNPh)_4$,[28] the Al–N–Al and N–Al–N angles were equal as required by the symmetry of the molecule. This trend could not be confirmed with $(MeAlNMes)_4$ since the differences are within the standard deviation of the angular values at Al and N. On the other hand, it is notable that in compound **5**, two of the three C–Al–N angles have an average value of 116.3 (1)° whereas the third C–Al–N angle has a larger average value of 141.0 (1)°. Similarly, the three C–N–Al angles have the average values 115.9 (2), 122.7 (2), and 136.1 (2)°. A more detailed comparison with $(PhAlNPh)_4$,[28] $[HAlN(i\text{-}Pr)]_4$,[29] and $[MeAlN(i\text{-}Pr)]_4$[29] was not possible since only the mean distances were reported in the two former molecules and imposed symmetry excluded the latter.

Thermolysis of Gallanes. The close structural similarity between the aluminum and gallium precursors **1**–**5** might have led to the prediction that further heating would have led to similar products in the case of gallium compounds. The aminogallanes have, however, demonstrated a much greater preference for methane elimination via C–H activation over elimination via capture of N–H hydrogen (Scheme I). For example, although the reaction between $AlMe_3$ and H_2NDipp gave the trimeric $(MeAlNDipp)_3$ (**6**) compound, the parallel reaction with $GaMe_3$ gave compound **7**, in which the *o*-isopropyl methyl group on the aryl ring becomes bonded to gallium. Similarly, whereas the reaction between $AlMe_3$ and H_2NMes gave the cubic species $(MeAlNMes)_4$ (**8**), the parallel reaction with $GaMe_3$ gave isomers **9** and **10** demonstrating a preference for activation of the *o*-methyl C–H bond on mesityl. Cyclometalations in aluminum and gallium chemistry via C–H activation have, of course, been reported[42–44] previously, but, with the exception of the work in ref 9, no work has appeared on amides. The structures of **7**, **9**, and **10** are, apparently, the first reported structures of this type for gallium.

On the basis of the results of these parallel reactions, it is unlikely that the amino gallanes undergo intramolecular cyclometalation for steric reasons. On the contrary, since gallium is slightly larger than aluminum, an intermolecular condensation reaction is more likely in the case of gallium since it is less hindered. Subtle differences in the reactivity and structure of similar aluminum and gallium compounds have been reported previously. For example, it has been reported that five-coordination is apparently a less stable geometry in gallium compounds than it is in the corresponding aluminum species.[45,46] In addition, the imino derivative $(\overline{\mathrm{CH_2CH_2NM}}\mathrm{Et_2})_n$ (M = Al, Ga) exists as a trimer (n = 3) when M = Al, whereas it is a dimer (n = 2) when M = Ga.[47] In another example, a study of the reaction of aluminum and gallium alkyls with terminal acetylenes revealed some surprising differences. Aluminum alkyls add to the triple bond of acetylenes resulting in a substituted alkene.[48] In contrast, gallium alkyls provoke the pseudo-acidic character of the terminal acetylene leading to nucleophilic attack of the alkyl on hydrogen and subsequent elimination of alkane.[48] The carbon–carbon triple bond remains intact. Clearly, there is adequate precedent for significantly different behavior in Al and Ga compounds. An alternative explanation of the difference in reactivity between Al and Ga compounds relates to the more electropositive nature of Al in comparison to Ga. The more electropositive metal (Al) favors intermolecular association and the concomitant N–H capture, whereas the less strongly electropositive (less Lewis acidic) Ga centers are less inclined to associate further. The lower Lewis acidity of Ga has been well-established in other derivatives.[14,18,48] A well-known manifestation of this phenomenon is the monomeric nature of $GaMe_3$ versus the dimeric nature of Al_2Me_6.

Acknowledgment. The financial support of the National Science Foundation is gratefully acknowledged. We also thank Dr. M. Olmstead and Prof. H. Hope for helpful advice and experimental assistance and Prof. W. H. Fink for making the data in Table II available prior to publication.

Supplementary Material Available: Full tables of atom coordinates, crystallographic data, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (47 pages); listing of structure factors (97 pages). Ordering information is given on any current masthead page.

---

(41) Perego, G.; Del Piero, G.; Cesari, M.; Zazetta, A.; Dozzi, G. *J. Organomet. Chem.* **1975**, *87*, 53.

(42) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 1501.

(43) Schmidbauer, H.; Wolfsberger, W. *J. Organomet. Chem.* **1969**, *16*, 188.

(44) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2976.

(45) Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 1036.

(46) Beattie, I. R.; Gilson, T.; Ozin, G. A. *J. Chem. Soc. A* **1968**, 1092.

(47) Storr, A.; Thomas, B. S. *J. Chem. Soc. A* **1971**, 3850.

(48) Eisch, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 3830.

Relative Aromaticity in Heteropolar Inorganic Analogues of Benzene

William H. Fink* and John C. Richards

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received September 27, 1990*

Abstract: Ab initio electronic structure calculations have been carried out on a series of heteropolar inorganic analogues of hydrocarbons in order to evaluate reaction energies for an isodesmic reduction by ethane and homodesmotic reactions as indicators of the relative aromaticities of the recently synthesized $X_3Y_3R_6$ rings where XY is BP and AlN. Calculations where XY is CC and BN are also reported to establish the scale. Optimized geometries and energies through RHF/6-31G* are reported for both reactions, and energies at the SCF optimized geometries including fourth-order Moller-Plesset perturbation corrections are reported for the homodesmotic reaction. The homodesmotic reactions are taken to be the most useful index and give the results with MP4(SDQ) of CC (22.1 kcal/mol) $\gg$ BP (12.7 kcal/mol) $\sim$ BN (11.1 kcal/mol) > AlN (1.9 kcal/mol).

Introduction

The recent synthesis of inorganic planar six-membered-ring molecules involving the heavier main group elements[1–3] draws attention to the issue of aromaticity and the utility of its possible extension to help in understanding the chemistry of these new

---

(1) Dias, H. V. Rasika; Power, Philip P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270–1271.

(2) Waggoner, Krista M.; Hope, Hakon; Power, Philip P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699–1700.

0002-7863/91/1513-3393$02.50/0 © 1991 American Chemical Society

Table I. $X_3Y_3H_6$ Planar Optimized Geometries[a]

X	Y	method	R_{XY}	R_{XH}	R_{YH}	α_{XYX}	α_{YXY}	α_{XYH}	α_{YXH}
B	P	RHF/STO-3G[b]	1.782	1.153	1.362	122.5	117.5	118.8	121.3
B	P	RHF/3-21G*[b]	1.841	1.182	1.383	123.2	116.9	118.4	121.6
B	P	RHF/6-31G*[b]	1.852	1.183	1.383	123.2	116.8	118.4	121.6
Al	N	RHF/STO-3G	1.734	1.475	1.019	126.6	113.4	116.7	123.3
Al	N	RHF/3-21G*	1.789	1.589	1.010	124.6	115.4	117.7	122.3
Al	N	RHF/6-31G*	1.791	1.584	1.003	125.3	114.7	117.4	122.6
B	N	RHF/STO-3G[c]	1.418	1.161	1.019	122.8	117.2	118.6	121.4
B	N	RHF/3-21G	1.441	1.190	1.001	122.4	117.6	118.8	121.2
B	N	RHF/6-31G*[d]	1.426	1.193	0.996	122.4	117.6	118.8	121.2
B	P	expt[e]	1.84			124.	115.		
B	N	expt[f]	1.436	1.258	1.050	121.1	117.7	119.4	121.2
Al	N	expt[g]	1.78			125.	115.		

[a] Distances in angstroms, angles in degrees. [b] The planar geometry is not a true minimum. Values reported are optimized under constraint for the molecule to be planar. [c] Results obtained agree with those reported by: Boyd, Russell J.; Choi, Sai Cheng; Hale, Christopher C. *Chem. Phys. Lett.* **1984**, *112*, 136–141. [d] Results obtained agree with those reported by: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. [e] Dias, H. V. Rasika; Power, Philip P. *J. Am. Chem. Soc.* **1989**, *111*, 144–148. Crystal structure of two highly substituted derivatives of boraphosphabenzene. [f] Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. In *Structure data of free polyatomic molecules*; Hellwege, K. H., Hellwege, A. M., Eds.; Springer: Berlin, 1976; Landolt-Bornstein, New Series, Group II, Vol. 7. [g] Waggoner, Krista M.; Hope, Hakon; Power, Philip P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699–1700. Crystal structure of $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$.

III-V compounds. The new rings that have been synthesized all have bulky substituents attached which may be important in stabilizing the ring. Ab initio electronic structure calculations on the parent ring systems can help to unravel the intrinsic nature of the rings themselves and will be useful in future considerations of the influence of substituents. An important contribution to the understanding of these rings and their relationship to aromatic organic molecules that ab initio calculations can offer is some estimate of the resonance energy of the ring.

Quantification of the resonance energy in aromatic molecules has been elusive. One of the reasons for this is that the concept of aromaticity was originally introduced to account for the reactivity preference of substitution over addition, and any index generated from molecular ground-state properties alone necessarily only approximates the condition of the reactants at the critically important point along the reaction path. In addition it is difficult to isolate only the electronic structure delocalization without simultaneously introducing other electronic and nuclear structural changes in model reaction sequences. Considerable progress was made in reconciling these difficulties when Dewar and de Llano[4] discovered that there was an underlying additive value of single and double bond strengths in the heats of formation of linear polyenes. By using as a reference the hypothetical linear acyclic polyene composed of the same number of additive units of single and double bonds as in the compound of interest, an extremely useful index of resonance energy could be calculated. Hess and Schaad[5,6] and Hess, Schaad, and Holyoke[7,8] showed that the new reference worked equally well in the simpler Huckel theory to bring consonance between the calculated resonance energy, which has become known as DRE, and accepted relative experimental aromaticities. Gutman, Milun, and Trinajstic[9] and Aihara[10] have elaborated on the relationship between DRE and fundamental topological relationships of the nuclear structure using graph theory to define a topolgical resonance energy or TRE that parallels the DRE.

All electron calculations of reaction energies have also focused on the reference compounds, but have emphasized the importance of trying to establish equal errors in the neglected parts of the calculation on both sides of a reaction. Hehre, Ditchfield, Radom, and Pople[11] and Radom, Hehre, and Pople[12] suggested that reactions with equal numbers of formal bonds on each side of the reaction, termed isodesmic reactions, would minimize the known difficulties in correctly calculating bond dissociation energies and therefore could be extremely useful in considerations of relative thermodynamics. George, Trachtman, Bock, and Brett[13] suggested that a further constraint on the isodesmic reactions that would maintain equal numbers on both reaction sides of similarly hybridized atoms and equal numbers of atoms with zero, one, two, or three hydrogens attached would be particularly useful in calculations of resonance energies. Reactions meeting these two conditions were termed homodesmotic. A series of papers by these authors[14-18] elaborated the advantages of the choice of homodesmotic reactions for use in establishing delocalization energies and demonstrated the similarity in trend of resonance energies for homodesmotic reactions and the older DRE and TRE indices. Their work, using both experimental heats of formation and ab initio total energy calculations, also shows good agreement between the calculated ab initio values and the values derived from heats of formation. Homodesmotic reactions have consequently received much attention in providing a quantitative estimate of resonance energies in hydrocarbons.[19-23] Sax and Janoschek[24] have extended

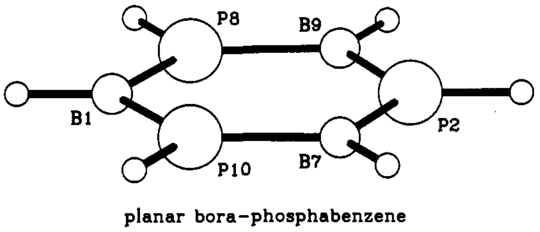

Figure 1. A perspective drawing of the planar constrained optimized geometry of $B_3P_3H_6$. The BP bond distances are 1.85 Å, the BH distances are 1.18 Å, and the PH distances are 1.38 Å.

---

(3) Dias, H. V. Rasika; Power, Philip P. *J. Am. Chem. Soc.* **1989**, *111*, 144–148.

(4) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789–795.

(5) Hess, B. Andes, Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305–310.

(6) Hess, B. Andes, Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907–3912.

(7) Hess, B. Andes, Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1972**, *28*, 3657–3667.

(8) Hess, B. Andes, Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1975**, *31*, 295–298.

(9) Gutman, Ivan; Milun, Milorad; Trijajstic, Nenad *J. Am. Chem. Soc.* **1977**, *99*, 1692–1704.

(10) Aihara, Jun-ichi *J. Am. Chem. Soc.* **1976**, *98*, 2750–2758.

(11) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(12) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

(13) George, Philip; Trachtman, Mendel; Bock, Charles W.; Brett, Alistair M. *Theor. Chim. Acta* **1975**, *38*, 121–129.

(14) George, Philip; Trachtman, Mendel; Brett, Alistair M.; Bock, Charles W. *J. Chem. Soc., Perkin Trans. II* **1976**, 1036–1047.

(15) George, Philip; Trachtman, Mendel; Bock, Charles W.; Brett, Alistair M. *J. Chem. Soc., Perkin Trans. II* **1976**, 1222–1227.

(16) Bock, Charles W.; George, Philip; Trachtman, Mendel *J. Mol. Struct.* (*Theochem*) **1984**, *109*, 1–16.

(17) Bock, Charles W.; George, Philip; Trachtman, Mendel *J. Phys. Chem.* **1984**, *88*, 1467–1472.

(18) George, Philip; Bock, Charles W.; Trachtman, Mendel *Tetrahedron Lett.* **1985**, *26*, 5667–5670.

Table II. Complete Geometries for All Molecules (All Distances Are in Angstroms and All Angles in Degrees)

analogue	molecule	parameter	STO-3G	3-21G*	6-31G*
ethylene	BH_2PH_2	r(BP)	1.726	1.796	1.808
		r(BH)	1.154	1.184	1.184
		r(PH)	1.358	1.380	1.380
		∠(HBH)	120.63	122.27	123.18
		∠(HPH)	109.58	110.55	110.19
	AlH_2NH_2	r(AlN)	1.717	1.765	1.771
		r(AlH)	1.474	1.588	1.583
		r(NH)	1.016	1.005	0.998
		∠(HAlH)	124.17	122.66	123.20
		∠(HNH)	108.65	111.01	110.15
transoid butadiene	$B_2P_2H_6$	r(B=P)	1.747	1.812	1.825
		r(B—P)	1.814	1.861	1.872
		r(BH) external H	1.156	1.185	1.185
		r(BH) internal H	1.154	1.183	1.183
		r(PH) external H	1.357	1.379	1.379
		r(PH) internal H	1.362	1.386	1.385
		∠(HBH)	119.68	121.42	122.15
		∠(HPH)	110.53	111.86	111.54
		∠(BPB)	126.69	124.94	125.10
		∠(PBP)	125.04	124.65	124.55
		∠(HBP) internal H	117.52	117.66	118.16
		∠(HBP) internal H	115.85	116.53	116.45
	$Al_2N_2H_6$	r(Al=N)	1.725	1.776	1.781
		r(Al—N)	1.735	1.795	1.794
		r(AlH) external H	1.476	1.589	1.584
		r(AlH) internal H	1.471	1.584	1.579
		r(NH) internal H	1.021	1.013	1.005
		r(NH) external H	1.016	1.004	0.998
		∠(HALH)	122.08	121.40	121.86
		∠(HNH)	108.71	110.72	109.96
		∠(AlNAl)	131.89	129.60	131.63
		∠(NAlN)	118.66	119.95	120.06
		∠(HAlN) internal H	121.75	120.39	120.53
		∠(HNAl) internal H	113.88	115.52	114.75
staggered ethane	BH_3PH_3	r(BP)	2.011	2.008	2.023
		r(BH)	1.158	1.204	1.205
		r(PH)	1.374	1.390	1.390
		∠(BPH)	117.69	117.27	117.43
		∠(PBH)	103.59	103.87	103.18
	AlH_3NH_3	r(AlN)	1.998	2.044	2.096
		r(AlH)	1.483	1.609	1.603
		r(NH)	1.030	1.011	1.005
		∠(AlNH)	112.54	109.20	111.10
		∠(NAlH)	99.44	100.32	99.46
chair cyclohexane	$B_3P_3H_{12}$	r(BP)	1.943	1.968	1.987
		r(BH$_a$)	1.155	1.202	1.202
		r(BH$_e$)	1.156	1.199	1.200
		r(PH$_a$)	1.373	1.393	1.395
		r(PH$_e$)	1.371	1.390	1.390
		∠(PBP)	109.36	108.23	108.34
		∠(BPB)	120.12	117.43	118.45
		τ(PBPB)	44.14	50.80	49.01
		∠(H$_a$BP)	107.71	106.39	106.38
		∠(H$_e$BP)	109.21	110.76	110.42
		∠(H$_a$PB)	109.26	109.98	109.90
		∠(H$_e$PB)	108.20	108.74	108.34
	$Al_3N_3H_{12}$	r(AlN)	1.889	1.949	1.965
		r(AlH$_a$)	1.474	1.594	1.589
		r(AlH$_e$)	1.479	1.606	1.600
		r(NH$_a$)	1.029	1.016	1.008
		r(NH$_e$)	1.029	1.020	1.010
		∠(NAlN)	101.70	106.43	105.96
		∠(AlNAl)	121.56	121.70	125.33
		τ(NAlNAl)	54.99	46.85	40.80
		∠(H$_a$AlN)	108.81	108.49	108.05
		∠(H$_e$AlN)	107.19	106.31	106.42
		∠(H$_a$NAl)	109.44	109.27	108.31
		∠(H$_e$NAl)	106.26	104.77	104.28

the use of the homodesmotic reaction energy to inorganic compounds in their pseudopotential study of resonance energy in Si_6H_6.

Other ab initio work on six-membered planar rings of inorganic elements includes additional work on Si_6H_6,[25-27] borazine and

---

(19) Schulman, Jerome M.; Disch, Raymond L. *J. Am. Chem. Soc.* **1984**, *106*, 1202–1204.

(20) Haddon, R. C.; Raghavachari, Krishnan *J. Am. Chem. Soc.* **1985**, *107*, 289–302.

(21) Rice, Julia E.; Lee, Timothy J.; Remington, Richard B.; Allen, Wesley D.; Clabo, D. Allen, Jr.; Schaefer, Henry F. III *J. Am. Chem. Soc.* **1987**, *109*, 2902–2909.

(22) Disch, Raymond L.; Schulman, Jerome M. *Chem. Phys. Lett.* **1988**, *152*, 402–403.

Table III. Total Energies[a]

X	Y	method[b]	$X_3Y_3H_6$	$X_3Y_3H_{12}$	$X_2Y_2H_6$	XYH_6	XYH_4
B	P	HF/3	-1 094.391 362	-1 097.884 544	-730.702 305	-367.069 402	-365.909 486
B	P	HF/6	-1 099.708 687	-1 103.211 313	-734.255 568	-368.853 655	-367.689 920
B	P	M4/6	-1 100.330 919		-734.677 196	-369.090 676	-367.906 991
Al	N	HF/3	-888.134 706	-891.602 661	-593.176 334	-298.284 572	-297.135 377
Al	N	HF/6	-892.767 585	-896.242 690	-596.284 850	-299.847 840	-298.696 091
Al	N	M4/6	-893.454 632		-596.755 411	-300.107 596	-298.938 198
B	N	HF/3	-239.842 576		-160.986 852		-81.043 436
B	N	HF/6	-241.151 008		-161.868 315		-81.489 101
B	N	M4/6	-241.897 109		-162.380 706		-81.754 249
C	C	HF/6	-230.703 137	-234.207 99[c]	-154.919 651	-79.228 26[d]	-78.031 718
C	C	M4/6	-231.492 063		-155.462 815		-78.310 549
C	C	HF/3	-229.419 445	-232.916 907	-154.059 454	-78.793 948	-77.600 988

[a] Energies in hartrees at SCF optimized geometries. $X_3Y_3H_6$ is the planar ring analogue of benzene; $X_3Y_3H_{12}$ is the chair conformer of the analogue of cyclohexane; $X_2Y_2H_6$ is the transoid conformer of the analogue of butadiene; and XYH_6 and XYH_4 are the analogues of staggered ethane and ethylene, respectively. [b] HF is Hartree-Fock; M4 is Moller-Plesset 4th-order perturbation theory with single, double, and quadruple excitations; basis sets 3-21G* and 6-31G* are abbreviated to 3 and 6, respectively. [c] Schulman, Jerome M.; Disch, Raymond L. *J. Am. Chem. Soc.* **1984**, *106*, 1202-1204. [d] Bock, Charles W.; George, Philip; Trachtman, Mendel *J. Mol. Struct.* **1984**, *109*, 1-16.

Table IV. Homodesmotic Reaction Energies

		ΔE_{rxn}, kcal/mol	
reaction	RHF 3-21G*// RHF 3-21G*	RHF 6-31G*// RHF 6-31G*	MP4SDQ 6-31G*// RHF 6-31G*
$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3CH_2{=}CHCH{=}CH_2$	27.6	24.7	22.1
$B_3N_3H_6 + 3BH_2{=}NH_2 \rightarrow 3BH_2{=}NHBH{=}NH_2$	7.7	8.4	11.1
$B_3P_3H_6 + 3BH_2{=}PH_2 \rightarrow 3BH_2{=}PHBH{=}PH_2$	8.1	7.4	12.7
$Al_3N_3H_6 + 3AlH_2{=}NH_2 \rightarrow 3AlH_2{=}NHAlH{=}NH_2$	1.8	0.8	1.9

[a] The first line of the column headings indicates the approximation level of the calculation. The second line indicates the approximation level, the optimized geometry of which was used for the calculation.

Table V. Isodesmic Hydrogen Transfer Reaction

	ΔE_{rxn},[a] kcal/mol	
reaction	RHF 3-21G*// RHF 3-21G*	RHF 6-31G*// RHF 6-31G*
$C_6H_6 + 3CH_3CH_3 \rightarrow 3CH_2{=}CH_2 + C_6H_{12}$	51.1	53.2
$B_3P_3H_6 + 3BH_3PH_3 \rightarrow 3BH_2{=}PH_2 + B_3P_3H_{12}$	-8.4	-7.2
$Al_3N_3H_6 + 3AlH_3NH_3 \rightarrow 3AlH_2{=}NH_2 + Al_3N_3H_{12}$	-12.8	-12.5

[a] Calculations are reported for the optimized geometries consistent with each level of approximation reported.

related molecules,[28-30] and P_6.[31] We report here results of calculations on benzene, borazine, boraphosphabenzene, and alumazine and the necessary smaller molecules to enable calculation of homodesmotic reaction energies for comparison of resonance in this series of compounds. We have also included comparison of isodesmic reduction by ethane which is more analogous to the older reactions of hydrogenation for characterization of resonance energy.

Results and Discussion

All calculations were performed with the Gaussian series of programs[32] by using standard keyword choices for methods, basis sets, and options. Molecular geometry specification used Z-matrix approaches that maintained point group symmetries for the idealized geometries. Table I displays the optimum geometric parameters for the D_{3d} six-membered rings of general formula $X_3Y_3H_6$ along with experimental values from compounds containing these rings. There is generally excellent agreement between the experimental values and the optimized ones. Figure 1 is a perspective drawing of the optimized geometry of $B_3P_3H_6$ as illustrative of these ring compounds.

These optima were verified by vibrational frequency calculations with the 6-31G* basis set. The AlN and BN compounds were established as true local minima on the surface. The BP compound showed three degrees of freedom that had imaginary frequencies; all three were out-of-plane vibrations. The planar constraint on this compound was relaxed, and a true minimum found of energy -734.264 189 3 hartree, 8.6 mhartree or about 5 kcal/mol lower in energy. Nevertheless, we have used the energy of the optimized planar form in establishing the energetic indices of aromaticity for the boraphosphabenzene because the synthesized compounds do have the planar structure, perhaps imposed by the substituents on the ring, and for consistency with the other compounds of the series.

Table II lists the geometric parameters at optimization for the other compounds required for calculation of the reaction energies used as measures of aromaticity, and Table III gives the energies calculated at the optimum geometries given by Tables I and II. The ethane analogues in the table were optimized as the staggered conformer, the butadiene analogues were planar transoid conformers, and the cyclohexane analogues were all chair conformers. The cisoid conformer for the AlN analogue of butadiene was 0.46 mhartree lower in energy than the transoid form for the 6-31G*

---

(23) Lee, Timothy J.; Rice, Julia E.; Remington, Richard B.; Schaefer, Henry F. III *Chem. Phys., Lett.* **1988**, *150*, 63-70.

(24) Sax, Alexander F.; Janoschek, Rudolf *Phosphorous Sulfur* **1986**, *28*, 151-166.

(25) Sax, A. F.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651.

(26) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(27) Clabo, D. A.; Schaefer, H. F. III *J. Chem. Phys.* **1986**, *84*, 1664.

(28) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(29) Boyd, Russell J.; Choi, Sai Cheng; Hale, Christopher C. *Chem. Phys. Lett.* **1984**, *112*, 136-141.

(30) Doiron, C. E.; Grein, F.; McMahon, T. B.; Vasudevan, K. *Can. J. Chem.* **1979**, *57*, 1751-1757.

(31) Nagase, Shigeru; Ito, Keiji *Chem. Phys. Lett.* **1986**, *126*, 43-47.

(32) Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fleuder, E. M.; Pople, J. A. *Gaussian 82*; Carnegie-Mellon University: Pittsburgh, 1983. Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Rhagavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh PA, 1984. *Gaussian 88*; Gaussian, Inc.: 4415 Fifth Avenue, Pittsburgh, PA 15213.

Table VI. Measures of Bond Polarity and π Orbital Only Mulliken Populations[c]

Bond Polarity

		$X_3Y_3H_6$		XYH_4		
XY	basis	X net[a]	Y net[a]	X net[a]	Y net[a]	XYH_4 dipole[b]
BP	3-21G	−0.235	0.193	−0.065	0.019	0.930
BP	3-21G*	−0.052	−0.034	−0.010	−0.106	1.225
BP	6-31G*	−0.012	−0.045	0.042	−0.082	1.049
AlN	3-21G	1.248	−1.315	0.739	−0.960	1.413
AlN	3-21G*	0.878	−1.042	0.685	−0.972	1.541
AlN	6-31G*	0.929	−1.133	0.719	−1.082	1.193
BN	3-21G	0.746	−1.011	0.385	−0.893	2.005
BN	6-31G*	0.474	−0.781	0.265	−0.858	1.821
CC	3-21G	−0.239	−0.239	−0.425	−0.425	0.0
CC	6-31G*	−0.199	−0.199	−0.353	−0.353	0.0

Mulliken Populations[c]

		$X_3Y_3H_6$		XYH_4	
XY	basis	X elects	Y elects	X elects	Y elects
BP	6-31G*	0.378	3.616	0.281	3.707
BP	3-21G	0.395	3.605	0.286	3.713
BP	3-21G*	0.420	3.572	0.311	3.685
AlN	6-31G*	2.217	1.726	2.150	1.818
AlN	3-21G	2.282	1.718	2.198	1.802
AlN	3-21G*	2.273	1.662	2.190	1.774
BN	6-31G*	0.305	1.667	0.243	1.740
BN	3-21G	0.360	1.640	0.291	1.708
CC	3-21G	1.000	1.000	1.000	1.000
CC	6-31G*	0.990	0.990	0.992	0.992

[a] Net charge on the atom as calculated by nuclear charge minus total Mulliken population. [b] Values in debye. [c] π and σ densities are not separated by symmetry in calculations reported for basis sets with polarization functions.

basis set; again we decided to use the transoid form for consistency among the series, and further in this case the difference in calculated values is unimportant.

Tables IV and V present the results of ΔE_{rxn} for the homodesmotic and isodesmic hydrogen transfer reactions, respectively. It is possible to calculate experimental values for these reactions for the hydrocarbon cases[33] to estimate the reliability of the calculations. They are 21.2 kcal/mol for the homodesmotic reaction and 48.7 kcal/mol for the isodesmic reaction. There is excellent agreement between the ab initio value and the experimantal data for the homodesmotic reaction. When the concept of the homodesmotic reaction was first introduced by George, Trachtman, Bock, and Brett[13] as a measure of aromaticity, they observed that it generally gave the same trend of relative aromaticity as that of the DRE and TRE indices and that there was good reason to expect the errors on both sides of the equation for calculated energies to be approximately equal. Both reactions establish the same relative order for the degree of aromaticity in these inorganic analogues of benzene, namely CC ≫ BP ~ BN > AlN. However, the sign of the isodesmic reaction energy would put these compounds on the antiaromatic side of the scale.

The homodesmotic reaction energy results are to be preferred on a number of points as discussed at length by George, Trachtman, Bock, and Brett.[13-18] The homodesmotic reaction maintains greater similarity of bond types on both sides of the reaction because it requires equal numbers of the same kinds of hybrids. Arising naturally from the constraint of equal numbers of hybrids, the homodesmotic reaction is more sharply focussed on the difference in delocalization between adjacent double bonds. Also while isodesmic reactions are designed to minimize correlation errors, they are not always successful, particularly in reactions involving heteropolar bonds, and we have not calculated the isodesmic energy differences at a correlated level.

Table VII. Vibrational Frequencies Calculated for RHF/6-31G*

		$B_3N_3H_6$ planar	$B_3P_3H_6$ planar	$Al_3N_3H_6$ planar	$B_3P_3H_6$ nonplanar[a]	
A′	1	911.9	435.5	476.7	326.8	
	2	1003.4	700.8	635.4	593.4	
	3	1123.2	806.3	639.5	844.0	
	4	1299.3	861.0	906.8	877.4	
	5	1427.2	1012.9	1090.7	1005.0	
	6	2741.5	2738.9	2025.8	2673.1	
	7	3860.6	2810.0	3781.3	2784.3	
A″	1	405.1	215.2i	217.4	153.4	
	2	766.3	500.9	505.6	554.2	
	3	1023.1	745.4	661.6	786.4	
E′	1	554.3	282.4	256.9	229.4	233.1
	2	991.1	667.1	602.1	639.9	697.2
	3	1141.9	828.0	797.4	804.9	805.6
	4	1496.9	1007.2	924.8	1031.1	1015.1
	5	1593.0	1145.5	1139.4	1164.4	1144.6
	6	2728.1	2739.9	2014.6	2673.9	2675.6
	7	3862.1	2807.8	3782.9	2788.3	2790.4
E″	1	295.9	175.7i	143.5	195.1	210.2
	2	740.4	323.8	501.2	440.0	441.5
	3	1004.7	829.3	593.6	825.5	827.7

[a] The symmetry designations are no longer appropriate for the nonplanar species. A best effort to match the kinds of motion as defined by the normal mode vectors was made.

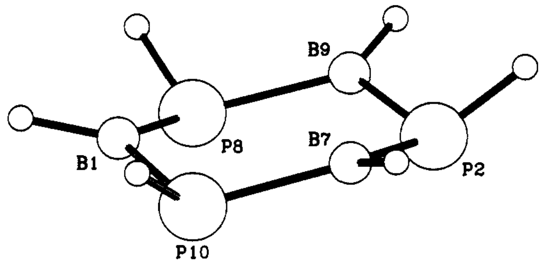

Figure 2. A perspective drawing of the nonplanar optimized geometry of $B_3P_3H_6$. The B_9–P_8 and B_7–P_{10} bonds are 1.94 Å, while other B–P bond distances are 1.87 Å. The P–H distances are 1.39 Å and the B–H distances are 1.18 Å.

Table VI presents some measures of polarity of the XY bonds taken from the calculations. The upper part of the table displays the net charge ascribed by Mulliken population analysis to the atoms for both the planar six-membered rings and the ethylene analogue molecule. Also reported is the total molecular dipole moment calculated for the ethylene analogue. There is more electronic charge attributed to the more electropositive element in the heteropolar six-membered-ring compounds than is attributed to that atom in the ethylene analogue. The order of bond polarity in the heteropolar rings is AlN > BN > BP, which is the inverse of the aromaticity attributed by the homodesmotic reaction. Increased electronegativity differences causing greater bond polarity will lead to greater localization and hence decreased aromaticity. The lower half of the Table VI shows the results of Mulliken population analysis applied only to the p-orbitals oriented perpendicular to the molecular plane, the π electrons. The increase in the number of π electrons on the more electropositive atom in the six-membered-ring compounds over that of the ethylene analogue completely parallels the trend in net atomic charge in the upper half of the table. These parallel trends support the expectation that the delocalization of the π electrons around the ring is largely responsible for the net electron shift toward the more electropositive atom. A related aspect of the AlN compound that may be affecting its stabilization energy is the disparity in the atomic radii of Al and N. A large difference in atomic radii will lead to inadequate electron sharing and hence less delocalization.

Table VII reports the vibrational frequencies calculated at the optimized geometries. Both the BN and AlN compounds exhibit all real vibrational frequencies at the planar geometry, but the

---

[33] Heats of formation at 0 K taken from *TRC Thermodynamic Tables Hydrocarbons*, Thermodynamics Research Center, Texas Engineering Experiment Station, The Texas A&M University System, College Station TX 77843-3111, April 30, 1989.

BP compound exhibits imaginary frequencies for the lowest energy vibration in the nondegenerate A″ and doubly degenerate E″ modes. The eigenvectors for these two modes are out-of-plane puckering motions. Also reported in Table VII are the frequencies for the BP compound obtained when the dihedral angles maintaining the ring's planarity were permitted to relax, a new optimum obtained, and the resulting nonplanar geometry shown in Figure 2 was used in a frequency calculation. This nonplanar optimum can be described as a puckered ring with an elongated middle between the two three-atom ends. One end is a PHBHPH piece while the other is a BHPHBH piece. The BP distance between the pieces is 1.935 Å, while the BP distances within both end pieces is 1.866 Å. The PH distances increased somewhat compared with the planar constrained form to 1.392 Å, but the BH distances are essentially unchanged at 1.185 Å. The calculated frequencies are all real for this structure, demonstrating that it is a true minimum, but we have made no effort to establish that it is the absolute minimum. The preference of the BP compound for the puckered ring is closely related to the preference of PH_2BH_2 to pyramidalize at phosphorus as reported by Allen, Scheiner, and Schaefer.[34] For the puckered ring, the out-of-plane angle at each of the phosphorus atoms is about 60°, while that at boron is ten times smaller or about 6°. Allen, Scheiner, and Schaefer[34] report 70 and 6° respectively for the out-of-plane angles in PH_2BH_2.

Conclusion

Ab initio electronic structure calculations systematically investigating a hierarchy of basis sets and including correlation effects via perturbation theory have been applied to assist in understanding the chemistry of the recently synthesized heteropolar III-V analogues of benzene. The rich literature investigating aromaticity in organic molecules led us to rely most heavily upon the use of homodesmotic reaction sequences to establish an aromatic index for these compounds. An isodesmic hydrogen transfer reaction corroborates the relative trend of aromaticity, but would differ in its attribution of antiaromaticity to all of the heteropolar compounds. The attribution of antiaromaticity to compounds whose experimental behavior is aromatic has been a common deficiency in many reaction sequences suggested for indices of aromaticity, but the homodesmotic scheme appears to be more satisfactory in this regard. The relative aromaticity established by the homodesmotic reaction energy for the six-membered-ring analogues of benzene is CC $\gg$ BP $\sim$ BN $>$ AlN. The BP compound is calculated to prefer a nonplanar geometry pyramidal at phosphorus as has been previously reported for the ethylene analogue BH_2PH_2. The bulky substituents on the ring of the synthesized BP compounds may be playing a role in keeping the planar geometry.

Acknowledgment. We would like to acknowledge stimulating discussions with Philip Power and Krista Waggoner throughout the course of this work. The work was performed largely on the Data General MV/10000 computer which was purchased with the aid of NSF Grant CHE 8420185. Additional computing resource was made available at the San Diego Supercomputer Center and The Office of Academic Computing at UCLA. We would also like to acknowledge Wesley Allen for conversations about homodesmotic reactions and Ed Motell for enabling a calculation on the CSU Multiflow Trace facility.

---

[34] Allen, Thomas L.; Scheiner, Andrew C.; Schaefer, Henry F. III *Inorg. Chem.* **1990**, *29*, 1930–1936.

New Synthetic Approach to Extended Solids: Selective Synthesis of Iron Silicides via the Amorphous State

Thomas Novet and David C. Johnson*

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403.
Received September 10, 1990

Abstract: A new synthetic approach in which thin (15–50 Å) amorphous elemental layers are sequentially deposited to create a unique initial reactant is described. This new approach overcomes the limitations of traditional, diffusion-limited, solid-state synthetic methods, which offer no control of the reaction pathway and therefore no control over which intermediates are formed. In our synthetic approach, the initial layered composite is diffused at low temperatures to produce a homogeneous amorphous alloy; nucleation is then the rate-limiting step in the formation of a crystalline material. The layered nature of the starting reactant permits the reaction to be followed in a quantitative manner with use of X-ray diffraction. The composition-directed crystallization of iron silicides from homogeneous amorphous alloy intermediates is described as a first example of our new synthetic method. The resultant iron silicides all crystallized below 550 °C, including Fe_5Si_3, which is metastable with respect to a mixture of FeSi and $FeSi_3$ below 825 °C.

Introduction

Many of the basic principles and concepts used by molecular chemists only apply to a small fraction of solid-state compounds. An example of one of these principles is the law of definite proportions, the concept that a compound has a definite stoichiometry. Nonstoichiometric extended solids such as FeO_x with $1.05 < x < 1.13$ are common to many solid-state phase diagrams. Another example is the ability of molecular chemists to predict the structure and reactivity of an unknown compound based on a knowledge of the bonding and coordination of the atoms involved. Except for simple derivative compounds based upon simple chemical substitution, the ability to predict the structures of new solid-state compounds is practically impossible due to the large variability in coordination numbers found in extended solids. The concept of a reaction mechanism is another well-developed principle of molecular chemistry. Its usefulness in solid-state synthesis has been limited, since most solid-state synthetic techniques produce thermodynamic products. Also, most solid-state synthesis techniques do not permit the course of a reaction to be followed. It is the concept of a reaction mechanism that we will expand in this paper and apply to the synthesis of extended solids.

The synthetic strategies involved in the preparation of molecular compounds are directed at controlling the kinetics of chemical reactions. Chemists adjust experimental conditions so as to optimize the fraction of starting material that reacts along the desired kinetic pathway. In contrast, the synthetic strategies directed at