

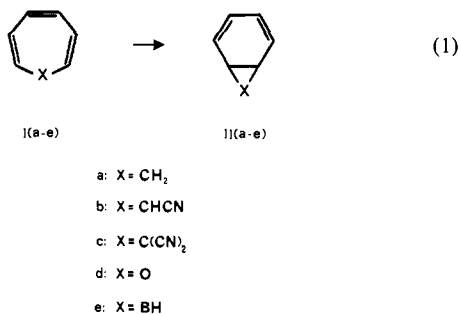
Energetics of Valence Isomerization in Seven-Membered Rings. Cycloheptatriene-Norcaradiene and Related Rearrangements

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Abstract: Ab initio molecular orbital theory is applied to the isomerizations of cycloheptatriene to norcaradiene, cyano-cycloheptatrienes to cyanonorcaradienes, oxepin to benzene oxide, and borepin to boranorcaradiene. The enthalpy of norcaradiene is estimated to be 5.5 kcal/mol greater than that of cycloheptatriene at 0 K. Good agreement with experiment is obtained for enthalpies of reaction where comparisons are possible. With use of model compounds, it is argued that the effect of cyanalation on the norcaradiene-cycloheptatriene energy difference is complex, involving perturbations on both systems, especially cycloheptatriene. New evidence for the aromatic character of borepin is adduced.

The rearrangement of 1,3,5-cycloheptatriene (CHT) (Ia), also known as tropilidene, to bicyclo[4.1.0]hepta-2,4-diene (norcaradiene, NCD) (IIa) is a subject of long-standing experimental¹ and theoretical² interest. Although IIa has recently been synthesized,^{1f} its equilibrium concentration in solution is quite small.^{1c} This implies that in the near future experimental determinations of ΔH and ΔG for this reaction will be based on deductions drawn from model compounds; an accurate theoretical treatment of this and the following related problems is therefore of value. It is



known that substitution of cyano groups at the 7-position of CHT decreases the energy of isomerization: 7-cyano substitution gives rise to very small amounts of 7-CN-NCD as observed by NMR³ and 7,7-(CN)₂ substitution leads almost exclusively to 7,7-(CN)₂NCD.⁴ During the course of this work, measurements of ΔG in solution for the mono- and dicyano cases, b and c, have been made.³ While the role of cyclopropane-CN conjugation in NCD has been discussed by Hoffmann,⁵ the effects of cyanide upon the isomerization energy also involve CHT, as described in the Discussion.

For the oxepin-benzene oxide rearrangement (Id), a ΔH of -1.7 kcal/mol has been determined.⁶ The last reaction in the series, borepin (Ie) \rightarrow boraNCD (IIe), has been the subject of recent theoretical studies:⁷ although neither system is known, borepin

derivatives have been synthesized and boraNCD derivatives suggested as intermediates. The present calculations indicate a substantial ΔH value for this endothermic reaction, in agreement with the earlier work.

The method proceeds by two steps. In the first, ΔH 's for reactions 1b-e are related to that of reaction 1a by using what we call "exchange" reactions. Then, ΔH for reaction 1a is determined from isodesmic⁸ and homodesmic⁹ reactions.

Method of Calculation

Ab initio calculations on I and II (a-e) were made at the STO-3G (SCF), 4-31G (SCF), 4-31G (RMP2), and 6-31G* (SCF) levels, using *C_s* symmetry; in the monocyano case, only the exo compounds were studied. For CHT, NCD, oxepin, and benzene oxide 6-31G* (RMP2) calculations were made as well. The geometries were optimized at the STO-3G level and for NCD and CHT at the 3-21G level as well with use of GAUSSIAN 80;¹⁰ calculations in the larger basis sets at these geometries were performed with machine-code optimized programs written by us (The Queens College Quantum Chemistry Package). All RMP2 calculations utilize the frozen-core approximation. The 6-31G* (SCF) root mean square Cartesian forces for NCD and CHT are ca. 0.005 au in both STO-3G and 3-21G geometries, implying that the optimization of these structures at the 6-31G* level will not significantly change their energy differences.

Geometries

The monocyclic molecules Ia-d are tub shaped, whereas borepin is planar. STO-3G geometric parameters of CHT and borepin have been reported previously;^{7a} those for oxepin are given in Table I, which also contains the 3-21G values for CHT. The oxepin geometry improves upon the partially optimized planar STO-3G structure reported in an interesting paper by Hayes et al.^{2a} We find bow and stern elevation angles of 49.6° and 24.1°, respectively, which are similar to the corresponding STO-3G values found for CHT,⁷ 47.7° and 27.3°. An X-ray structure determination of 3,7-di-*tert*-butyl-5-phenyl-2-*p*-tolylloxepin furnished bow and stern values of 62.4° and 29.3°, respectively,¹¹ suggesting that steric perturbations on the bow angle of this system are large.

The STO-3G geometrical parameters of NCD and benzene oxide are given in Table I, parameters for boraNCD having been reported previously;^{7b} the 3-21G parameters of NCD are also given in Table I. NCD has a boat structure with bow and stern angles

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Table I. Geometrical Parameters of NCD, CHT, Benzene Oxide, and Oxepin^a

parameter ^b	NCD ^c	CHT	benzene oxide	oxepin
Bond Lengths (Angstroms)				
C ₁ A	1.509 (1.515)	1.526 (1.513)	1.440	1.413
C ₁ C ₂	1.500 (1.476)	1.318 (1.325)	1.497	1.316
C ₂ C ₃	1.321 (1.327)	1.483 (1.460)	1.324	1.488
C ₃ C ₄	1.480 (1.466)	1.325 (1.334)	1.477	1.322
C ₁ C ₆	1.524 (1.523)		1.504	
C ₁ H ₁	1.083 (1.072)	1.084 (1.074)	1.089	1.084
C ₃ H ₂	1.083 (1.073)	1.084 (1.075)	1.083	1.081
C ₃ H ₃	1.082 (1.072)	1.085 (1.075)	1.083	1.080
C ₇ H _{7x} ^d	1.080 (1.071)	1.089 (1.082)		
C ₇ H _{7e}	1.080 (1.069)	1.089 (1.088)		
Bond Angles (Degrees)				
AC ₁ C ₂	118.4 (119.0)	123.3 (122.6)	117.2	124.9
C ₁ C ₂ C ₃	121.4 (121.5)	125.3 (125.2)	120.8	126.1
C ₂ C ₃ C ₄	121.8 (121.7)	125.9 (125.9)	121.8	123.8
C ₁ AC ₆	60.6 (61.2)	110.3 (110.0)	63.0	109.7
H ₁ C ₁ C ₂	116.1 (116.4)	119.9 (119.6)	116.8	121.1
H ₂ C ₂ C ₃	121.6 (121.3)	115.2 (115.7)	121.7	115.9
H ₄ C ₄ C ₃	117.1 (117.0)	118.5 (118.1)	116.9	119.1
H _{7x} C ₇ C ₁	117.6 (116.8)	110.1 (110.2)		
H _{7e} C ₇ C ₁	118.2 (117.3)	109.4 (109.3)		
H _{7e} C ₇ H _{7x}		107.6 (107.8)		
Dihedral Angles (Degrees)				
C ₁ C ₂ C ₃ C ₄	4.8 (7.1)	33.3 (33.6)	6.3	29.8
C ₂ C ₃ C ₄ C ₅	0.0 (0.0)	0.0 (0.0)	0.0	0.0
C ₂ C ₁ AC ₆	-106.0 (-105.3)	-60.0 (-61.9)	-106.7	-63.1
AC ₁ C ₂ C ₃	63.6 (61.3)	3.3 (3.9)	60.6	6.8
H ₁ C ₁ C ₂ C ₃	-152.5 (-152.6)	-176.7 (-176.1)	-157.3	-176.4
H ₁ C ₁ C ₂ H ₂	28.4 (27.5)	0.0 (0.0)	22.3	-0.8
H ₄ C ₄ C ₃ C ₂	177.3 (175.2)	175.2 (174.9)	175.1	-178.7
H _{7x} C ₇ C ₁ H ₁	2.1 (1.0)	-1.7 (-3.5)		
H _{7e} C ₇ C ₁ H ₁	-141.8 (-143.9)	-120.0 (-121.8)		
Elevation Angles (Degrees)				
bow	71.1 (70.3)	47.7 (49.5)	73.2	49.6
stern	4.8 (6.9)	27.3 (27.6)	6.2	24.1

^aOptimized in the STO-3G and 3-21G basis sets; the latter values are in parentheses. ^bThe following numbering system has been employed to simplify the table: (1) the symbol A represents C₇ of NCD and CHT and O of benzene oxide and oxepin; (2) the oxepin numbering is consecutive around the ring beginning at a carbon adjacent to oxygen; (3) hydrogens bear the same subscripts as their adjacent carbons; (4) subscripts x and e indicate exo and endo hydrogens, respectively. ^cIn 7,7-(CN)₂NCD the calculated C₁C₇ and C₁C₆ bond lengths are 1.544 and 1.507 Å, respectively. ^dIn the STO-3G optimization C₇H_{7x} and C₇H_{7e} bond lengths were constrained to be the same.

of 71.1° and 4.8° in STO-3G and 70.3° and 6.9° in 3-21G. Similar values were found in the X-ray structures of several 7,7-disubstituted NCD's:¹² bow angle = 68.5–71.9° and stern angle = 4.2–7.0°. A comparison can be made between the X-ray structure of 2,5-dimethyl-7,7-dicyanonorcaradiene¹³ and the STO-3G optimized structure of 7,7-(CN)₂NCD. The calculated bond lengths and bond angles agree with their X-ray counterparts to within 0.03 Å and 3°, respectively, which is the accuracy expected at the STO-3G level; also, the two compounds differ in their 2,5-substituents.

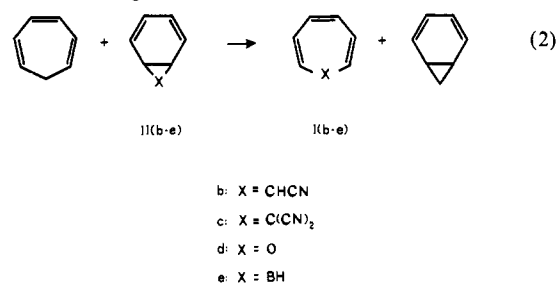
The calculated C₁C₇ exceeds C₁C₆ by 0.037 Å, which is in accord with the X-ray difference for the (slightly dissymmetric) dimethyldicyanonorcaradiene, 0.043–0.048 Å, (in cyanocyclopropane the corresponding difference is 0.029 Å¹⁴). C₁C₆ is larger than C₁C₇ by 0.015 Å in NCD. The effect of cyano substitution is to shorten the opposing CC bond and to lengthen the adjacent bonds relative to their counterparts in NCD. The origin of this effect has been attributed by Hoffmann⁵ to transfer of electrons,

within a bonding molecular orbital, from C₁C₆ antibonding and C₁C₇ bonding Walsh hybrid atomic orbitals into the cyano π system.

The geometry of benzene oxide is similar to that of NCD, with bow and stern angles of 73.2° and 6.2°, respectively. The present geometry improves upon a partially optimized STO-3G structure,^{2a} which is 3.2 kcal/mol higher in energy.

Energies

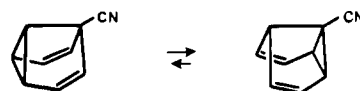
Exchange Reactions. Table II contains the ab initio energies of I and II, a–e, at the various levels of calculation. The 6-31G* energies of NCD and CHT optimized in the STO-3G basis are in good agreement with those reported in a footnote by Cremer et al.^{2b} Since reactions 1 are neither isodesmic nor homodesmic, it is not surprising that use of the differences in the ab initio energies leads to significant scatter in the calculated ΔH's. For example, use of the energies in Table II gives ΔH values for reaction 1a of -8.0, 10.7, 11.1, 5.7, and 1.8 kcal/mol. The STO-3G bias in stability toward the cyclopropane compounds pervades the series a–e and is well-known. The disparity between the 6-31G*(SCF) and 6-31G*(RMP2) values for CHT → NCD, however, is a new result which demonstrates the difficulty in the calculation of non-isodesmic isomer energies. This can be alleviated to a considerable extent for cases b–e through use of the hypothetical exchange reactions 2b–e which balance the same



numbers of single and double bonds and rings. This could allow significant cancellation of the ab initio errors as well as errors due to neglect of the unknown differences in zero-point energies. Thus, a knowledge of ΔH for any one of reactions 1 furnishes accurate estimates of ΔH of the others.

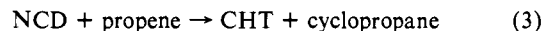
A necessary but not sufficient condition for this scheme to work is the stability of the ΔH values for reactions 2 with respect to the change in the level of calculation; the ultimate justification, of course, lies in comparison with experiment. From Table III, it is clear that the ΔH values are stable, the ranges for reactions 2b–e being only 0.9, 1.1, 6.8, and 1.6, respectively. The greatest variation is found for the oxepin–benzene oxide case, which probably reflects the fact that reactions 2d (and also 2e) are not isodesmic.

It is interesting to note that exchange reaction 2b bears a strong resemblance to the cyanosemibullvalene rearrangement studied by Paquette and Volz.¹⁵



Since the reactant and product of this reaction are analogues of the products and reactants of reaction 2b, it is not surprising that ΔH of reaction 2b, 4.0 kcal/mol, is similar to the ΔG value estimated for the reverse of the semibullvalene rearrangement, 2.4 kcal/mol.¹⁵

Calculation of the CHT–NCD Energy Difference. Consider next the calculation of the CHT–NCD energy difference. There are sufficient thermochemical data to form an isodesmic reaction involving Ia and IIa at 0 K:



It is necessary to ignore the difference in zero-point energies in

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Table II. Ab Initio Energies (hartrees)

molecule ^a	ab initio energy ^{b,c}				
	STO-3G	4-31G(SCF)	4-31G(RMP2)	6-31G*(SCF)	6-31G*(RMP2)
CHT	-266.4064	-269.2941	-269.9108	-269.6805 ^d	-270.5630
NCD	-266.4191	-269.2771	-269.8931	-269.6714 ^d	-270.5600
7-CN-CHT	-356.9493	-360.8801	-361.7013	-361.4098	
7-CN-NCD	-356.9694	-360.8704	-361.6896	-361.4071	
7,7-(CN) ₂ CHT	-447.4832	-452.4495	-453.4813	-453.1205	
7,7-(CN) ₂ NCD	-447.5100	-452.4482	-453.4779	-453.1258	
oxepin	-301.6638	-305.0408	-305.6871	-305.4841	-306.4110
benzene oxide	-301.6878	-305.0243	-305.6763	-305.4818	-306.4186
borepin	-252.8116	-255.5718	-256.1441	-255.9336	
boraNCD	-252.7707	-255.5023	-256.0727	-255.8733	

^aCHT = 1,3,5-cycloheptatriene (tropilidene); NCD = bicyclo[4.1.0]hepta-2,4-diene (norcaradiene). ^bEnergies at the STO-3G optimized geometries assuming C_s symmetry. ^cRMP2 calculations were performed in the frozen-core approximation. ^dThe corresponding energies of CHT and NCD at their 3-21G optimized geometries are -269.6817 and -269.6721.

Table III. Heats of Reaction for Reactions 2b-e, 3, and 4 (kcal/mol)^a

reaction	STO-3G	4-31G(SCF)	4-31G(RMP2)	6-31G*(SCF)	6-31G*(RMP2)
2b	4.6	4.6	3.7	4.0	
2c	8.8	9.9	9.0	9.0	
2d	7.1	0.3	4.3	4.3	6.6
2e	-33.7	-33.0	-33.7	-32.1	
3	4.3	2.6	1.5	2.0 (2.2) ^b	1.7 (1.9) ^b
4				4.3 ^c	5.5 ^c

^aOn the basis of STO-3G geometries unless otherwise noted. ^bOn the basis of 3-21G geometries for NCD, CHT, cyclopropane, and propene. ^cOn the basis of 6-31G* geometries except for NCD and CHT, where 3-21G geometries were used.

Table IV. Heats of Reactions for I → II (kcal/mol) at 0 K

reaction	STO-3G	4-31G(SCF)	4-31G(RMP2)	6-31G*(SCF)	6-31G*(RMP2)	expt
(1a) CHT → NCD	3.1 ^a	4.8 ^a	5.9 ^a	5.2 ^a (4.3) ^c	5.5 ^a (5.5) ^c	6.2 ^d
(1b) 7-CN-CHT → 7-CN-NCD ^b	0.9	0.9	1.8	1.5		2.0 ^d
(1c) 7,7-(CN) ₂ CHT → 7,7-(CN) ₂ NCD ^b	-3.3	-4.4	-3.5	-3.5		-3.2 ^d
(1d) oxepin → benzene oxide ^b	-1.6	5.2	1.2	1.2	-1.1	-1.7 ^e
(1e) borepin → boraNCD	39.2	38.5	39.2	37.6		

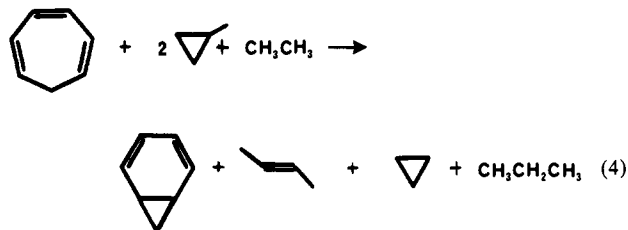
^aComputed from the heats of reaction 3 and experimental $\Delta H_f^\circ(0\text{ K})$'s; 3-21G geometries were used at the 6-31G* levels. ^bComputed from the heats of reaction 2, Table III, using 5.5 kcal/mol for CHT → NCD. ^cComputed from the 6-31G* heats of reaction 4 and experimental $\Delta H_f^\circ(298\text{ K})$'s. ^dEnthalpies of reaction calculated from the free energies of Anet and Miura³ after making corrections for entropies of reaction and for the effects of *tert*-butyl substitution in the case of reaction 1a. ^eReference 6.

eq 3 since the zero-point energy of NCD is not known; however, it is encouraging that the difference in zero-point energies of propene and cyclopropane is small, only 0.9 kcal/mol.^{16,17} When the energies of cyclopropane and propene calculated at their STO-3G geometries were used, the energies for reaction 3 given in Table III were found; with the exclusion of results in the STO-3G basis, which has known deficiencies for strained systems, the range of ΔH values is only 1.1 kcal/mol. These ΔH values can be used with the known heat of reaction at 0 K (assuming fixed nuclei) for propene → cyclopropane, 7.4 kcal/mol,¹⁷ to give the following heats of reaction for reaction 1a at 0 K (in kcal/mol): 4.8 at 4-31G(SCF), 5.9 at 4-31G(RMP2), 5.4 at 6-31G*(SCF), and 5.7 at 6-31G*(RMP2).

The NCD and CHT geometries have also been optimized in the 3-21G basis. The 3-21G value of ΔH is 4.4 kcal/mol, which leads to a ΔH for reaction 1a of 3.0 kcal/mol. However, the STO-3G and 3-21G basis sets are much better for geometries than for energies; for example, the 3-21G basis gives 14.2 kcal/mol for the isomerization energy of propene to cyclopropane,¹⁸ whereas the experimental value is 7.4 kcal/mol. In contrast, the 6-31G* isomerization energy when the 3-21G geometries are used is 8.2 kcal/mol,¹⁹ in good agreement with experiment. The 6-31G*(SCF) and (RMP2) calculations for reaction 3 at the 3-21G

geometries yield ΔH values for 1a of 5.2 and 5.5 kcal/mol, respectively: these are probably preferable to the 6-31G*/STO-3G values.

The NCD-CHT isomerization energy can also be calculated from reaction 4, which balances the same numbers of bonds of each type: methyls, methylenes (both alicyclic and cyclopropyl), and vinyl groups, as well as cyclopropane rings. There are reported 6-31G* energies for ethane,¹⁸ propane,¹⁸ cyclopropane,¹⁸ and



trans-2-butene;²⁰ we have optimized the geometry of methylcyclopropane in the 6-31G* basis set. Since the required experimental heats of formation for reaction 4 are only available at 298 K,²¹ we use them and ignore the enthalpy correction for reactants and products from 298 to 0 K (ca. 1 kcal/mol^{14c}) as well as the zero-point energy correction. The 6-31G*(SCF) and -(RMP2) calculations furnish CHT-NCD isomerization energies of 4.3 and 5.5 kcal/mol, respectively.

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(21) The ΔH_f° values employed (kcal/mol) were the following: methylcyclopropane, 5.7; *trans*-2-butene, -2.99; cyclopropane, 12.7; propane, -25.02; ethane, -20.04.

Table V. Dipole Moments (D) in the 4-31G and 6-31G* Basis Sets

molecule	4-31G(SCF)	6-31G*(SCF)	expt
NCD	0.5	0.5	
CHT	0.3	0.3	0.25 ^a
7-CN-NCD	4.6	4.6	
7-CN-CHT	4.4	4.4	
7,7-(CN) ₂ NCD	5.9	5.8	4.8 ^b
7,7-(CN) ₂ CHT	5.5	5.5	
benzene oxide	3.0	2.5	
oxepin	2.2	1.7	
boraNCD	0.7	0.6	
borepin	2.0	1.9	

^aButcher, S. S. *J. Am. Chem. Soc.* **1965**, *42*, 1833. ^bReference 4.

Since the zero-point energy corrections and the enthalpy changes from 298 to 0 K cannot be adequately assessed at this time, the most satisfactory estimate we can make, using the 6-31G*(RMP2) values from reactions 3 and 4, is that the enthalpy of NCD exceeds that of CHT by 5.5 ± 2 kcal/mol. A recent determination²² of ΔH_f° of CHT gave the value 44.6 kcal/mol, therefore the ΔH_f° of NCD is approximately 50.1 kcal/mol.

Isomerization Energies of Reactions 2b–e. We now turn to the calculation of ΔH for reactions 1b–e. When the heats of reaction for reactions 2b–e given in Table III are combined with the 5.5 kcal/mol value for $\text{CHT} \rightarrow \text{NCD}$, the ΔH values for these isomerizations are found (Table IV). It can be seen that the reaction $7\text{-CN-CHT} \rightarrow 7\text{-CN-NCD}$ is endothermic by 1.5 kcal/mol, while in the dicyano case, reaction 1c, the reaction is exothermic by 3.5 kcal/mol. The effects of cyanation on lowering the heats of reaction are nearly additive: -4.0 for one (exo) cyano group and -9.0 kcal/mol for two cyano groups. It might be noted that the dipole moments of the NCD form are only 0.2 to 0.3 D higher than the CHT form for both the parent and mono and dicyano cases. Therefore, solvent effects on these reactions should be small.

For the case of oxepin \rightarrow benzene oxide, the reaction is found to be slightly exothermic with ΔH equal to -1.1 kcal/mol at 6-31G*(RMP2); the experimental value in a non-polar solvent is -1.7 kcal/mol.⁶ From Table V it can be seen that the dipole moment of benzene oxide is greater than that of oxepin by ca. 0.8 D, in accord with its known preferential stabilization in polar solvents. It is likely, therefore, that the gas-phase ΔH , to which these calculations correspond, would be algebraically larger than -1.7 kcal/mol.

The conversion of borepin to boraNCD is highly endothermic, ΔH being on the order of 37 kcal/mol. This result argues for the aromatic character of borepin⁷; of course, part of the large ΔH arises because the CBC angle is more favorable for a trigonal boron in the borepin form. Oxepin adopts a tub conformation which is nearly isoenergetic with benzene oxide; planar oxepin would be an antiaromatic system.

Discussion

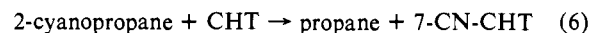
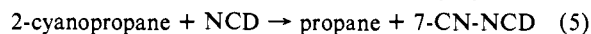
There are only indirect determinations of the CHT–NCD isomerization energy, based on model compounds, with which our theoretical value can be compared. The kinetic analyses of Warner and Lu¹⁶ furnish a $\Delta G(373\text{ K})$ of 4.0–4.5 kcal/mol for 7-alkylbenzoate derivatives of CHT and NCD. Assuming -2 eu for ΔS of reaction 1b in analogy with similar systems,³ a ΔH of 2.9–3.4 kcal/mol is obtained. Since it appears that substitution on the 7-position lowers the NCD–CHT gap,³ there is reasonable agreement between the theoretical value for CHT–NCD and that of the Warner–Lu system. A recent study by Anet and Miura³ of 2,5-di-*tert*-butyl-substituted CHT and NCD found a $\Delta G(223\text{ K})$ of 3.1 kcal/mol. Their model studies of the effects of the *tert*-butyl substitutions suggest that they lower ΔG for the isomerization by about 3.5 kcal/mol. Assuming a $T\Delta S$ contribution of -0.4 kcal/mol at this temperature, the experimental ΔH can be inferred to be 6.2 kcal/mol, which is in good agreement with

the present finding, 5.5 ± 2 kcal/mol. In contrast, the MINDO/3 method gives an isomerization energy of 12.2 kcal/mol;^{2a} results with the MNDO method are somewhat better, 8.3 kcal/mol (this work), although not as good as with the ab initio method.

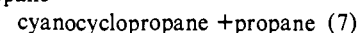
For $7\text{-CN-CHT} \rightarrow 7\text{-CN-NCD}$ the calculations furnish a ΔH of 1.5 kcal/mol. Anet and Miura³ have obtained a $\Delta G(193\text{ K})$ of 2.4 kcal/mol. Assuming, again, a ΔS of -2 eu, the ΔH can be estimated to be ca. 2.0 kcal/mol, which compares well with the calculated gas-phase value. Although the present calculations were performed only for the exo isomers of CHT and NCD, the NMR experiments of Wehner and Gunther^{23a} and Takeuchi et al.^{23b} show the exo isomer of CHT to have a lower free energy than the endo form by only 0.38–0.48 kcal/mol; similarly, from studies on the 2,5-di-*tert*-butyl-7-cyano isomerization, Takeuchi et al.^{23c} suggested that the *endo*- and *exo*-7-CN-NCD's are also nearly isoenergetic.

Turning to the dicyano reaction (reaction 1c) the calculated ΔH is -3.5 kcal/mol. Anet and Miura³ find a $\Delta G(225\text{ K})$ of -2.7 kcal/mol. ΔH can be estimated to be -3.2 kcal/mol, in good agreement with the calculated gas-phase value.

It is useful to analyze the effects of monocyano and dicyano substitution to determine whether they are manifested predominantly through NCD, as is commonly assumed,⁵ or through CHT as well. Although the question is model dependent, the following argument may be of some interest. The homodesmotic reactions 5 and 6 permit comparison of the effects of cyano substitution on NCD and CHT, respectively, with that on propane. The

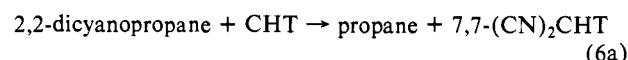
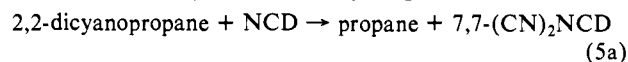


geometry of 2-cyanopropane was optimized at the 6-31G*(SCF) level leading to a conformation similar to that of propane. With use of the 6-31G* energies of propane, cyanopropane, CHT, and NCD, ΔH for reactions 5 and 6 was found to be -1.1 and 2.9 kcal/mol, respectively. This shows that relative to acyclic model compounds CHT is destabilized while NCD is stabilized (to a lesser extent) by cyano substitution. One source of the destabilization of CHT is repulsion between the π -electrons of the cyano group and those of carbons 1 and 6. The stabilizing effect of cyano substitution found in reaction 5 can also be found when NCD is replaced by cyclopropane, as in reaction 7. Here, the calculated

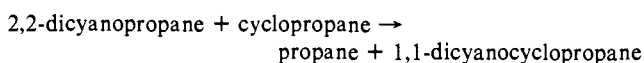


6-31G*(SCF) value is -2.0 kcal/mol, which is within experimental error of the value at 298 K, 0.9 kcal/mol.²⁴ Our interpretation of the effect of cyano substitution on the NCD–CHT equilibrium is then that the shift toward the NCD form arises from both stabilization of NCD and destabilization of CHT.

The dicyano case can be studied by constructing the homodesmotic reactions 5a and 6a for which the 6-31G*(SCF) ΔH values are -0.9 and 8.1 kcal/mol, respectively. Again, the destabilization



of CHT is more pronounced than the stabilization of NCD. The small ΔH of reaction 5a can be ascribed, in part, to the different levels of geometry optimization, since when the analogue to reaction 5a



was studied at the 6-31G*(SCF) level, with geometry optimization,

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a ΔH of -3.0 was found. However, although this enthalpy change is more negative than that of reaction 5a, it seems clear that stabilization of NCD alone is not sufficient to account for the 9.0-kcal/mol difference in energy of isomerization between the parent NCD-CHT system and its dicyano counterpart. Indeed, destabilization of CHT appears to be even more important.

Conclusion

The ab initio calculations reproduce the experimental heats of isomerizations, where known, quite well. In addition, the model calculations on cyano-containing compounds provide a new interpretation of the effect of cyano substitution upon the NCD-CHT equilibrium.

We emphasize that all the ΔH values computed here are for the gas phase at 0 K. While the corrections to 298 K may be

small, the solvent effects are influenced strongly by the difference in dipole moments of the two isomers, which is greatest in the case of benzene oxide-oxepin.

Acknowledgment. This research was supported in part by Grant No. 663228 from the PSC-CUNY Research Award Program of the City University of New York and a grant of computing time from the City University Committee on Research Computing. We thank Prof. F. A. L. Anet and S. S. Miura for several helpful discussions and for making results available before publication.

Registry No. Ia, 544-25-2; Ib, 13612-59-4; Ic, 92720-75-7; Id, 291-70-3; Ie, 291-62-3; IIa, 14515-09-4; IIb, 92720-76-8; IIc, 1618-16-2; IId, 1488-25-1; IIe, 79010-90-5; $\text{CH}_2=\text{CHCH}_3$, 115-07-1; CH_3CH_3 , 74-84-0; $\text{CH}_3\text{C}(\text{CN})_2\text{CH}_3$, 7321-55-3; methylcyclopropane, 594-11-6; cyclopropane, 75-19-4.

Valence-Shell Electron-Pair Repulsions: A Quantum Test of a Naive Mechanical Model

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Abstract: The repelling points-on-a-sphere representation of the valence-shell electron-pair repulsion (VSEPR) theory implies the form of the potential energy surface for bending deformations in molecules. The degree to which such a surface actually resembles the Born-Oppenheimer surface of molecular orbital theory was examined for tetrahedral and octahedral binary compounds by using extended-Hückel and, in some cases, ab initio computations. With few exceptions among the molecules studied, the results of the simple mechanical model simulated the quantum results in quadratic, cubic, and higher order force constants to a remarkable degree when pairwise additive potential functions were assumed to fall off as r_{ij}^{-n} . Parameter n characterizing the hardness of repulsions was approximately 4 for ab initio surfaces; EHT, imposing frozen VOIP, gave harder forces with $n \approx 6$. The present results show that the VSEPR model somehow captures the essence of molecular behavior to a degree heretofore not fully recognized.

Stereochemistry and molecular structure are accounted for quite successfully by a simple set of rules enunciated in the valence-shell electron-pair repulsion (VSEPR) theory.¹⁻³ According to this model the electron pairs (bond pairs and lone pairs) in the valence shell of a given main-group atom tend to be distributed in space in a way that imparts optimum mutual avoidance. A graphic representation often invoked is the likening of valence electron pairs to points-on-a-sphere (POS) that repel each other as if by some simple force law.³⁻⁶ Such a model invites the following question. If the POS model is a bona fide model for structure, working for nonspurious reasons, why should it not afford a realistic representation of the potential energy surface for bending displacements of molecules as well?

No very thorough investigation of this possibility has yet been conducted. Perhaps the main reason for this neglect is that the model is usually thought of as being so oversimplified, better suited for freshman chemistry courses than for research, that it would be absurd to attribute more to it than utility as a teaching device. Another reason is that surprisingly little about the systematics of potential energy surfaces for bending is known. With rare

exceptions, only quadratic constants for bending are available, and these are usually flawed by uncompensated effects of anharmonicity. Furthermore, in the most accurately studied cases, namely simple binary compounds AX_n , there are usually too few quadratic constants per molecule to provide the basis for a meaningful diagnosis in POS terms. For example, in AX_2 ($D_{\infty h}$), AX_4 (T_d), and AX_6 (O_h) molecules, there are only one, two, and three bending constants, respectively. Molecules with lower symmetry such as AX_5 (D_{3h}) with five constants, and AX_7 (D_{3h}), with seven, offer more interesting possibilities. Indeed, it was discovered, some time ago, once misassignments in the vibrational spectra had been corrected, that PF_5 ⁴ and IF_7 ⁶ do, in fact, exhibit characteristic POS aspects in the profiles of their quadratic bending constants. Furthermore, it was confirmed that the force law required to fit the IF_7 structure⁷ (a pentagonal bipyramid with coupled e_2'' and e_1' deformations) is the same as the force law required to fit the profile of quadratic constants.⁶

A much richer source of information that would allow a more definitive test of the POS force field lies in the pattern of the contours of potential surfaces. A standard representation of the pattern is the set of Taylor series expansion coefficients for displacements, including higher order (anharmonic) as well as quadratic force constants. Simple molecules have many more anharmonic constants than harmonic. Unfortunately, too little

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