and the anion. The carbanion is a much more effective donor than either the fluoro or oxyanion, and the methyl group rotates from the normal eclipsed, which offers only one acceptor hydrogen, to the staggered, which offers two acceptor hydrogens.

The preference of the aforementioned compounds for the cis isomer parallels the behavior of the dihaloethenes[45] and the halopropenes.[46] The phenomena has been termed the "cis effect",[47] and Crumb has invoked interactions involving permanent dipoles to account for this behavior.[48]

Conclusions

In this paper, we have examined the energies, structures, and intramolecular interactions in X=COR compounds. The calculated conformational preferences are in accord with experiment, where these are known. The decrease in bond angles that occurs when the conformations change from syn to anti have been rationalized in terms of orbital repulsions. In addition, these angle changes give rise to an increased lone pair–double bond conjugation in the syn conformation. While we find $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ interactions to be significant in magnitude, they are unimportant in determining the preferred conformations.

The six-electron pseudoaromatic interaction previously suggested as being responsible for the preferred conformation of methyl vinyl ether and related molecules either is absent or is insignificant. Instead, we propose intramolecular electrostatic interactions to be the most significant factor in determining the preferred conformation. This rationalization has been employed to explain both computational and experimental data for a wide variety of compounds, including vinyl sulfide, methyl vinyl sulfide, vinyl formate, the crotyl anion, and the halopropenes. Taken together with other reports in the literature,[36-38,44,45] the electrostatic effects appear to make a significant contribution in determining the preferred molecular conformation.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. Many of the calculations were performed on a Convex C1 computer, and we thank the Convex Computer Corporation for support. We express appreciation to Dr. Alan Reed for helpful discussions. We also thank Riverside City College for a sabbatical leave granted to D.B., which made this work possible.

Registry No. **1**, 107-25-5; **2**, 557-75-5; **4**, 123811-61-0; **5**, 123811-62-1; **6**, 77287-35-5; **7**, 74406-82-9; **8**, 77287-34-4; **9**, 74406-83-0; **10**, 64-18-6; **11**, 107-31-3.

Supplementary Material Available: Absolute energies and geometries of all species calculated here in GAUSSIAN 82 Archive Format (5 pages). Ordering information is given on any current masthead page.

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"Mixed Staffanes" as Intermediate-Length Staffs for Molecular-Size Tinkertoys. Parent Hydrocarbons and Terminal Diiodides Combining Bicyclo[1.1.1]pentane with Cubane or Bicyclo[2.2.2]octane Units

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Photochemically induced addition of [1.1.1]propellane across one or both of the C–I bonds in the 1,4-diiodocubane and 1,4-diiodobicyclo[2.2.2]octane yields doubly terminally functionalized straight molecules ("mixed staffanes") whose length is intermediate between those of the parent [*n*]staffanes differing by one in the value of *n*. Conversion to terminal dilithio derivatives and to the parent hydrocarbons is described, and a single-crystal X-ray structure of 1,4-bis(bicyclo[1.1.1]pent-1-yl)cubane is presented.

[*n*]Staffanes [***n***]**1**, the oligomers of [1.1.1]propellane **1**,[1,2] have been proposed as building block units for a molecular-size "Tinkertoy" construction set.[3,4] The facile synthesis, thermal stability, chemical inertness, transparency, straight linear geometry, and short-length increment of only $\sim 3^1/_3$ Å are the main advantages of these molecules. However, it is desirable to have staffs with intermediate lengths and otherwise similar properties. A way to achieve this would be to dope the staffs with rigid straight polycyclic units other than bicyclo[1.1.1]pentane. Inspired by the successful photochemical insertion of **1** into a variety of C–I bonds,[3,5] and particularly that of 1,3-diiodo[1]staffane, **2**, which yields 3,3′-diiodo[2]staffane, **3**, the photochemical reactions of 1,4-diiodocubane (**4**) and 1,4-diiodobicyclo[2.2.2]octane (**5**) with **1** were investigated.

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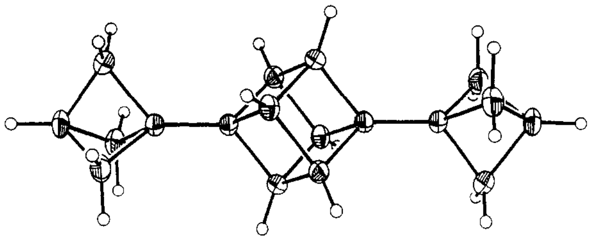
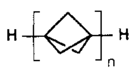


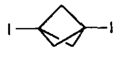
Figure 1. X-ray molecular structure of 1,4-bis(bicyclo[1.1.1]pent-1-yl)cubane (**8b**).

The synthesis and properties of the single- and double-insertion products and the conversion to their respective parent hydrocarbons are reported herein.

1



[*n*]1



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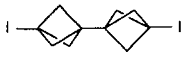

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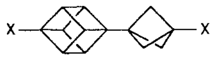

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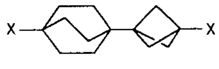

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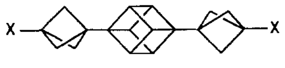

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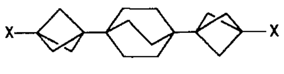


9

a: X = I
b: X = H

Results and Discussion

The diiodides **4**[6] and **5**[7] were photolyzed in benzene through a Pyrex filter with a medium-pressure mercury lamp at room temperature in the presence of **1** in pentane, prepared[2,8] from 1,1-bis(chloromethyl)-2,2-dibromocyclopropane by a method[3] that avoids contamination with ether. Depending upon the concentration of **1** and the length of irradiation, the single or the double adduct of **1** with **4** or **5** was the dominant product. Lower concentration of **1** and short irradiation times favored **6a** or **7a**. Longer irradiation times and higher concentration of **1** yielded **8a** and **9a**. No further addition of **1** across the C–I bond of **8a** and **9a** was observed upon extended irradiation with excess **1**.

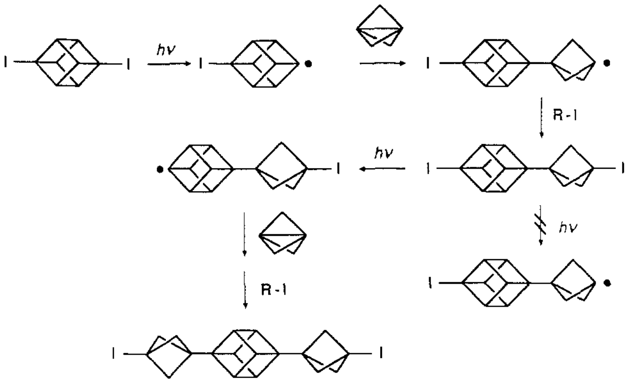
The diiodo derivatives are quite unstable, and analytically pure samples were not isolated. Samples for ^{1}H NMR spectroscopy were obtained by fractional sublimation. The parent hydrocarbons **6b**–**9b** were obtained by the reaction of **6a**–**9a** with *tert*-butyllithium at −78 °C in tetrahydrofuran, subsequently quenched with methanol. The facile formation of the dilithio derivatives bodes well for future conversion to other doubly terminally functionalized staffs.

A likely mechanism for the photochemical transformations is an initial dissociation of a C–I bond to a pair of radicals, followed by an addition of the bridgehead radical to **1**. The resulting radical can either abstract an iodine atom from the starting material, continuing a chain, or recombine with an I atom present in the solution. Scavenging of the latter by **1** is apparently inefficient since no **2** or **3** are observed among the products. The proposed reaction scheme thus is as follows:

Table I. H-to-H Length of Parent and Mixed Staffane Hydrocarbons

molecule	length, Å	mp, °C
[2]1	7.2[a]	32–33[b]
7b	7.9[c]	84–86
6b	8.1[d]	65–67
[3]1	10.44[b]	142–144[b]
9b	11.2[c]	204–206
8b	11.44	164–166
[4]1	13.74[b]	240–242[b]

[a] Estimated from the structure of methyl[2]staffane-3-carboxylate.[3a,10] [b] Reference 9. [c] Estimated from the structure[14] of bicyclo[2.2.2]octane-1,4-dicarboxylic acid. [d] Estimated from the structure of **8b**.



It is curious that the photoinduced insertion of **1** into a C–I bond of **4**, **5**, **6a**, and **7a** proceeds well but no further reaction of **8a** and **9a** with **1** is observed. A similar truncation of staff growth was observed in the analogous photochemical reaction of **1** with **2** to yield **3**, but no higher [*n*]staffane derivatives.[5] It appears as if a bridgehead C–I bond in bicyclo[1.1.1]pentanes often were stable with respect to photodissociation, with the exception of **2**, whose C–I bonds clearly interact, judging by a shift of the UV absorption peak relative to **3**.[5] A mechanistic study is needed before these puzzling observations are clarified.

A single-crystal X-ray structure of **8b** is shown in Figure 1. The molecule is linear, and the very short exocyclic bridgehead-to-bridgehead distance of 1.474 (3) Å is quite similar to those known in various [*n*]staffanes[3,4,9,10] and bicubyls.[11,12] It is readily understood in terms of hybridization effects (Bent's rules[13]).

The H-to-H molecular length of **8b** is compared with those of other staffanes in Table I. As we have not been able to grow suitable single crystals of **7b** or **9b**, the bicyclo[2.2.2]octane increment was approximated by adopting the value from the X-ray molecular structure of bicyclo[2.2.2]octane-1,4-dicarboxylic acid.[14] It is evident

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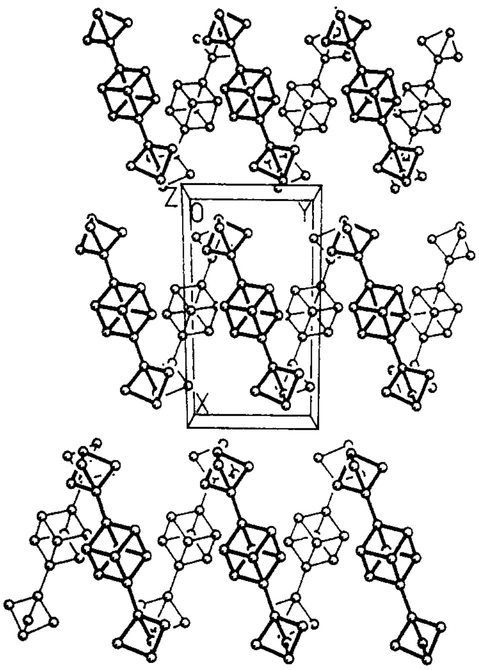

Figure 2. Packing diagram of **8b** projected along the *z* axis. Molecules drawn with thin bonds form a layer below the layer of molecules with thick bonds.

that the "mixed" staffanes reported presently indeed bridge the gap between [*n*]staffanes whose *n* values differ by unity and do so approximately equally, since the 1–4 separations in cubane and bicyclo[2.2.2]octane are very similar. This has interesting implications for their use as spacers in studies of electron and energy transfer, substituent effect attenuation, etc., in that it will permit a strict elimination of the effects of distance alone. In addition to the already available $3^1/_3$-Å increment, we now also have an ~1-Å increment between [*n*]staffane and its analogue with a single cubane or bicyclo[2.2.2]octane cage. From either one of these, there is an increment of ~2.3 Å to the next [*n*]staffane (Table I). Clearly, doping the staff with two such units can be expected to produce an approximately 2-Å increment relative to a parent [*n*]-staffane. Since doubly bridgehead-substituted bi(bicyclo[2.2.2]octyl) derivates are known,[15] an obvious extension of the present synthetic methodology should result in a collection of staffs with length increments of only about 1 Å up to nearly 16 Å of total H-to-H length.

The molecular packing diagram of **8b** is shown in Figure 2. Unlike the parent [*n*]staffanes,[9] this "mixed" staffane does not pack in a herring-bone fashion. The crystal is organized in alternating layers of parallel meshed molecules, whose axes are separated by 5.58 Å. The angle between the molecular alignment directions in neighboring layers is 38.6°.

Other properties of the "mixed" staffanes reflect their parentage. Their infrared spectra retain the characteristic frequencies due to the bicyclo[1.1.1]pentane as well as the cubane or bicyclo[2.2.2]octane groups. In particular, the characteristic intense CH_2 wagging vibration of the bicyclo[1.1.1]pentane units appears at its usual position near 1210 cm^{-1}, while the 836-cm^{-1} band in **8b** is characteristic of its cubane group. The NMR chemical shifts of these molecules are consistent with the previously reported values for staffanes,[3,5,9] bicubyls,[11,12] and bicyclo[2.2.2]octanes.[16] They are transparent in the UV at least down to 200 nm and are thermally fairly stable: the cubane-containing staffs up to 200–250 °C and those with a bicyclo[2.2.2]octane unit up to 280–300 °C, like [*n*]staffanes themselves.

Experimental Section

Melting points were determined in a sealed capillary with a Mel-Temp II apparatus and are uncorrected. NMR spectra were run in $CDCl_3$ on a GE-500 instrument. IR spectra were recorded on a Nicolet 60 SXR FTIR instrument. Mass spectra were taken on a 5995 Hewlett-Packard instrument.

Synthesis of 6b–9b. 1,4-Diiodocubane (**4**) or 1,4-diiodobicyclo[2.2.2]octane (**5**) (0.06 mmol) was dissolved in benzene (1.5 or 3 mL), and 2 mL of propellane in pentane (0.6 M) was added. The resulting mixture was irradiated through a Pyrex filter with a 450-W medium-pressure mercury lamp for 0.5–1 h. The reaction was followed by GC. After 0.5-h irradiation (3 mL of benzene) the major product was **6a** and **7a** respectively, and after 1 h (1.5 mL of benzene), **8a** or **9a**, respectively. Evaporation of the solvent and the excess propellane gave **6a**–**9a**. The mixture of **6a** and **8a**, or **7a** and **9a**, was dissolved in tetrahydrofuran (20 mL), and 0.24 mmol of 1.7 M *tert*-butyllithium in pentane was added at −78 °C. After 0.5 h of stirring at this temperature the mixture was quenched with methanol (1 mL). Evaporation of the solvent was followed by fractional sublimation yielding **6b** and **8b** or **7b** and **9b**. Analytical samples of **6b** and **9b** were obtained by preparative GC (10% SE 30).

1-(3-Iodobicyclo[1.1.1]pent-1-yl)-4-iodocubane (6a). Fractional sublimation of the mixture of **6a** and **8a** after 0.5-h irradiation gave 14 mg of **6a** (55%): ^{1}H NMR δ 2.22 (s, 6 H, 2′-H, 4′-H, 5′-H), 3.93 (m, 3 H, 2-H, 6-H, 8-H), 4.12 (m, 3 H, 3-H, 5-H, 7-H); MS *m*/*z* (relative intensity) 168 (19), 167 (70), 153 (77), 128 (42), 115 (24), 102 (20), 77 (34), 63 (54), 51 (100).

1,4-Bis(3-iodobicyclo[1.1.1]pent-1-yl)cubane (8a). Fractional sublimation of the mixture of **6a** and **8a** after 1-h irradiation gave 23 mg of **8a** (78%): ^{1}H NMR δ 2.22 (s, 12 H, 2′-H, 4′-H, 5′-H, 2″-H, 4″-H, 5″-H), 3.58 (s, 6 H, 2-H, 3-H, 5-H, 6-H, 8-H); MS *m*/*z* (relative intensity) 234 (8), 219 (9), 178 (15), 152 (13), 128 (18), 117 (100), 91 (38), 77 (40), 51 (60).

1-(3-Iodobicyclo[1.1.1]pent-1-yl)-4-iodobicyclo[2.2.2]octane (7a). Fractional sublimation of the mixture of **7a** and **9a** after 0.5-h irradiation gave 19 mg of **7a** (74%): ^{1}H NMR δ 1.49 (m, 6 H, 2-H, 6-H, 7-H), 2.08 (s, 6 H, 2′-H, 4′-H, 5′-H), 2.42 (m, 6 H, 3-H, 5-H, 8-H); MS *m*/*z* (relative intensity) 174 (2), 173 (15), 143 (4), 131 (21), 117 (25), 105 (29), 91 (77), 79 (100), 77 (89), 65 (43), 53 (57), 51 (50).

1,4-Bis(3-iodobicyclo[1.1.1]pent-1-yl)bicyclo[2.2.2]octane (9a). Fractional sublimation of the mixture of **7a** and **9a** after 1-h irradiation gave 24 mg of **9a** (81%): ^{1}H NMR δ 1.27 (s, 12 H, 2-H, 3-H, 5-H, 6-H, 7-H, 8-H), 2.08 (s, 12 H, 2′-H, 4′-H, 5′-H, 2″-H, 4″-H, 5″-H); MS *m*/*z* (relative intensity) 239 (2), 195 (8), 181 (11), 167 (15), 141 (17), 128 (28), 117 (66), 105 (48), 91 (100), 77 (75), 65 (47), 53 (31), 51 (31).

Bicyclo[1.1.1]pent-1-ylcubane (6b). The mixture of **6a** and **8a** with **6a** as a major product yielded 3 mg of **6b** (29%, based on 0.06 mmol of **4**): mp 65–67 °C; ^{1}H NMR δ 1.67 (s, 6 H, 2′-H, 4′-H, 5′-H), 2.52 (s, 1 H, 3′-H), 3.79 (m, 6 H, 2-H, 3-H, 5-H, 6-H, 7-H, 8-H), 4.03 (sep 1 H, 4-H); IR (CCl_4 or CS_2) 2968, 2905, 2869, 1218, 1211, 838 cm^{-1}; MS *m*/*z* (relative intensity) 153 (7), 128 (43), 115 (19), 91 (25), 77 (45), 65 (22), 53 (100).

1,4-Bis(bicyclo[1.1.1]pent-1-yl)cubane (8b). The mixture of **6a** and **8a** with **8a** as a major product yielded 6 mg of **8b** (42%, based on 0.06 mmol of **4**): mp 164–166 °C; ^{1}H NMR δ 1.66 (s, 12 H, 2′-H, 4′-H, 5′-H, 2″-H, 4″-H, 5″-H), 2.51 (s, 2 H, 3′-H, 3″-H), 3.56 (s, 6 H, 2-H, 3-H, 5-H, 6-H, 7-H, 8-H); ^{13}C NMR δ 28.3 (C-3′, C-3″), 42.9 (C-2, C-3, C-5, C-6, C-7, C-8), 47.6 (C-2′, C-2″, C-4′, C-4″, C-5′, C-5″), 49.1 (C-1′, C-1″), 58.9 (C-1, C-4); IR (CCl_4 or CS_2): 2968, 2906, 2871, 1218, 1191, 836 cm^{-1}; MS *m*/*z* (relative intensity) 165 (22), 153 (25), 141 (13), 128 (37), 115 (37), 103 (36), 91 (36), 77 (58), 65 (42), 51 (100).

1-Bicyclo[1.1.1]pent-1-ylbicyclo[2.2.2]octane (7b). The mixture of **7a** and **9a** with **7a** as a major product yielded 4 mg of **7b** (38%, based on 0.06 mmol of **5**): mp 84–86 °C; ^{1}H NMR

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δ 1.24 (m, 6 H, 2-H, 6-H, 7-H), 1.51 (m, 7 H, 3-H, 4-H, 5-H, 8-H), 1.51 (s, 6 H, 2′-H, 4′-H, 5′-H), 2.39 (s, 1 H, 3′-H); ^{13}C NMR δ 24.1 (C-4), 25.6 (C-3′), 25.8 (C-3, C-5, C-8), 27.0 (C-2, C-6, C-7), 29.2 (C-1), 46.4 (C-2′, C-4′, C-5′), 52.0 (C-1′); IR (CCl_4 or CS_2) 2960, 2931, 2903, 2858, 1294, 1197, 1133 cm^{-1}; MS *m/z* (relative intensity) 175 (1), 161 (5), 147 (33), 133 (14), 119 (31), 105 (68), 91 (100), 79 (85), 77 (38), 67 (68), 55 (31), 53 (27).

1,4-Bis(bicyclo[1.1.1]pent-1-yl)bicyclo[2.2.2]octane (9b). The mixture of **7a** and **9a** with **7a** as a major product yielded 9 mg of **9b** (62%, based on 0.06 mmol of **5**): mp 204–206 °C; ^1H NMR δ 1.24 (s, 12 H, 2-H, 3-H, 5-H, 6-H, 7-H, 8-H), 1.51 (s, 12 H, 2′-H, 2″-H, 4′-H, 4″-H, 5′-H, 5″-H), 2.39 (s, 2 H, 3′-H, 3″-H); ^{13}C NMR δ 25.7 (C-3′, C-3″), 27.2 (C-2, C-3, C-5, C-6, C-7, C-8), 29.8 (C-1, C-4), 46.5 (C-2′, C-2″, C-4′, C-4″, C-5′, C-5″), 51.8 (C-1′, C-1″); IR (CCl_4 or CS_2) 2962, 2934, 2907, 2869, 1309, 1200, 1134, 1047, 920 cm^{-1}; MS *m/z* (relative intensity) 213 (1), 201 (1), 185 (2), 173 (5), 159 (7), 145 (18), 131 (24), 119 (34), 105 (53), 91 (100), 79 (73), 67 (48), 53 (30).

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Registry No. 1, 35634-10-7; **4**, 97229-08-8; **5**, 10364-05-3; **6a**, 124381-06-2; **6b**, 124381-10-8; **7a**, 124381-07-3; **7b**, 124381-11-9; **8a**, 124381-08-4; **8b**, 124381-12-0; **9a**, 124381-09-5; **9b**, 124381-13-1.

Supplementary Material Available: Full details of the X-ray experiment, atomic positional and thermal parameters, bond lengths and angles, and a thermal ellipsoid plot showing the atom labeling scheme (10 pages); a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

Nucleophilic Substitution at Oxygen: The Reaction of PH_3 and NH_3 with H_3NO. An ab Initio Investigation

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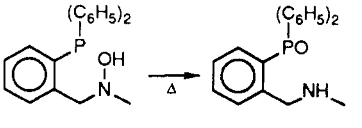
The oxygen transfer reaction between H_3NO and NH_3 or PH_3 is examined using ab initio calculations. The identity reaction involving H_3NO and NH_3 is calculated to have a barrier of 30.39 kcal mol^{-1} at HF/6-316*. This barrier increases to 37.34 kcal mol^{-1} with the inclusion of electron correlation through MP2. The N–O–N angle in the transition state is 180°, confirming a classical backside attack. The energy of reaction of H_3NO with PH_3 is calculated to be −65.5 kcal mol^{-1} with a barrier height of 30.5 kcal mol^{-1} at HF/6-31+G*//HF/6-31G*. The N–O–P angle in the transition state is 170.5°, suggesting that the reaction proceeds via the S_N2 mechanism. An early transition state is indicated by the reaction energetics and bond lengths. No stable intermediate was found for either reaction, confirming a single-step mechanism.

Geometric requirements of nucleophilic displacement reactions can be evaluated using systems which have the reacting centers tied together by a few intervening atoms. This linkage provides a cyclic transition state (TS) which imposes distinct restrictions upon the bond angles at the reacting center. Eschenmoser's classic experiments on the S_N2 reaction at carbon clearly established the requirement of a near linear arrangement of the nucleophile, carbon, and leaving group.[1] Similar studies have examined ring formation,[2] nucleophilic substitution at sulfur,[3] and displacement reactions at anionic nitrogen.[4] Beak and Loo recently examined displacement reactions at oxygen.[5] Their findings of first-order kinetics in reaction 1 suggest that this reaction does not proceed by the classic S_N2 mechanism. A linear arrangement of nucleophile and leaving group necessitates an intermolecular reaction and second-order kinetics for reaction 1. To further understand the mechanism of displacements at heteroatoms, we report ab initio calculations for a related reaction, reaction 2, which differs from reaction 1 by employing an *N*-oxide rather than a hydroxylamine. Reaction 2 is acyclic, but knowledge of the TS geometry in this reaction will indicate whether a cyclic intramolecular reaction is possible. We also examine the identity reaction between ammonia and ammonia oxide, reaction 3, to compare any difference between nitrogen and phosphorus as nucleophilic agents toward oxygen.



(1)

$$NH_3O + PH_3 \rightarrow NH_3 + PH_3O \qquad (2)$$

$$NH_3O + NH_3 \rightarrow NH_3 + NH_3O \qquad (3)$$

Computational Methods

All calculations were performed at the Hartree-Fock (HF) self-consistent field level using GAUSSIAN-86.[6] All structures were fully optimized within the constraints of the appropriate point group using the 3-21G,[7a] 3-21G(*),[6]

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