A Molecular Orbital Study of the Conformational Consequences of Stabilizing and Destabilizing Orbital Interactions in Hydrazine, Diphosphine, and Aminophosphine

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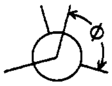
Abstract: Ab initio SCF-MO calculations have been performed at the 4-31G level for the rotational and pyramidal inversional processes in hydrazine, diphosphine, and aminophosphine. Extensive geometry optimization has been carried out in each case. Combination of the present results with related data from the literature leads to the following conclusions: (1) only the gauche conformation is a minimum on the rotational curve of hydrazine; (2) both gauche and anti conformations are minima on the rotational curve of diphosphine; (3) the dihedral angle in gauche diphosphine is 76°; (4) the pyramidal inversion barrier of hydrazine is slightly higher than that of ammonia; (5) the pyramidal inversion barrier of diphosphine is significantly lower than that of phosphine; (6) the "bisected" conformation is the transition state for pyramidal inversion in both hydrazine and diphosphine, but it is the ground state of aminophosphine; (7) nitrogen adopts a pyramidal configuration in the rotational transition state of aminophosphine; (8) the nitrogen inversion barrier is lower in aminophosphine than in ammonia; (9) the phosphorus inversion barrier is higher in aminophosphine than in phosphine. All of these observations are examined by a quantitative perturbational molecular orbital (PMO) analysis of the 4-31G wave functions, which takes into account both the stabilizing two-orbital two-electron and the destabilizing two-orbital four-electron orbital interactions between two AH_2 fragments or between an AH_2 and a BH_2 fragment. Useful insights into the factors responsible for the static and dynamic stereochemical properties of these molecules have thus been achieved. In particular, it has been possible to define, more clearly than in our previous work, the interrelationships between the PMO methodology and more classical concepts such as steric effects, dipole–dipole interactions, and electronegativity effects.

Introduction

Hydrazines and their congeners have attracted the attention of theoreticians, spectroscopists, and structural chemists for more than 4 decades.[3] However, despite the intense interest in such molecules, several aspects of their static and dynamic stereochemical properties are still uncertain. The concern with aminophosphines is more recent,[4] and, consequently, even less is known concerning these molecules.

Structural[5] and ab initio molecular orbital (MO) calculations[6] have established that the ground-state geometry of N_2H_4 is gauche, with a dihedral angle, ϕ, close to 90° (see **1**). A torsional itinerary about the N–N bond involves accessing the syn conformation ($\phi = 0°$), two enantiomeric gauche conformations (ϕ = 90 and 270°), and the anti conformation (ϕ = 180°). Ab initio theoretical estimates of the gauche–anti and gauche–syn barrier heights fall in the ranges 1.6–6.2 and 9.6–13.7 kcal/mol, respectively.[6] Unfortunately, the experimental value of 3.1 kcal/mol, obtained from microwave spectroscopy, was based on the incorrect assumption that the two barriers are equal.[5c]



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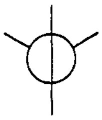
Microwave[7] and vibrational spectroscopic[8] investigations on P_2H_4 have revealed that this molecule adopts the gauche ground state conformation (**1**, $\phi = 74°$) in the vapor, liquid, and solid phases. An earlier structure determination by electron diffraction[9] was less definitive; nevertheless, the gauche conformation emerged as the preferred structure. Ab initio MO calculations have also been carried out on P_2H_4.[10] The most accurate study[10d] indicates that, as in the case of N_2H_4, the relative stabilities of the P_2H_4 conformations are gauche > anti > syn. However, in contrast to hydrazine, diphosphine is found to exhibit a local minimum at the anti conformation. Theoretical estimates[10d,e] of the gauche–anti and gauche–syn energy differences fall in the ranges 0.85–1.61 and 4.02–4.85 kcal/mol, respectively.

Somewhat less is known concerning pyramidal inversion in N_2H_4 and P_2H_4. Experimentally, the barrier to pyramidal inversion of N_2H_4 is known to be in the range 5.0–7.5 kcal/mol.[11] This compares favorably with the 6.1 and 7.4 kcal/mol values computed for the single pyramidal inversion process by ab initio[6g] and CNDO/2[12] procedures, respectively. There has been only one study[6f] of the rotation–inversion process in N_2H_4. Conformation **2** was calculated to be 11.99 kcal/mol more stable than conformation **3**. Theoretical information concerning pyramidal inversion in P_2H_4 is confined to one semiempirical estimate[12] (27.9 kcal/mol). Experimental data refer to the interconversion of a series of *dl* and racemic 1,2-diaryldiphosphines.[13] The barriers associated with this process (22.5–24.0 kcal/mol) were found to be significantly lower than those observed for the analogous tertiary phosphines[14] (29.7–35.6 kcal/mol). This observation has been interpreted[13] in terms of $p\pi$–$d\pi$ stabilization of the inversional transition state of diphosphines.



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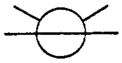

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The parent aminophosphine, H_2NPH_2, is as yet unknown. Its synthesis remains one of the challenges of inorganic chemistry. However, a significant number of experimental results have been accumulated regarding the stereochemistry

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Table I. Optimized Geometries, Total Energies, and Barriers Pertaining to the Pyramidal Inversion Process in PH_3

conformation	r_{P-H}, Å	∠XPH,[a] deg	total energy, au	inversion barrier, kcal/mol
pyramidal[b]	1.378	122.63	−338.636 41	61.35
planar[b]	1.345	90	−338.538 67	
pyramidal[c,d]	1.378	122.63	−342.021 84	33.41
planar[c,d]	1.345	90	−341.968 62	
pyramidal[d,e]	1.383	95	−342.025 69	34.61
planar[d,e]	1.345	90	−341.970 53	

[a] X was placed on the Z axis as a dummy atom; it represents the lone pair axis. [b] STO-3G calculations. [c] 4-31G (STO-3G) calculations. [d] See text for discussion. [e] 4-31G (4-31G) calculations.

Table II. Rotational and Pyramidal Inversion Barrier Data Computed for P_2H_4 by the 4-31G (STO-3G) Method[a]

conformation	r_{PP}, Å	∠HPH, deg	energy, au
1 ($\phi = 0°$)	2.200	95.75	−682.902 08
1 ($\phi = 60°$)	2.180	95.64	−682.906 65
1 ($\phi = 76°$)	2.179	95.68	−682.907 15
1 ($\phi = 90°$)	2.181	95.55	−682.907 07
1 ($\phi = 120°$)	2.180	95.00	−682.906 75
1 ($\phi = 180°$)	2.179	94.69	−682.907 12
2	2.096	96.07	−682.858 57
3	2.136	94.74	−682.849 71

[a] r_{PH} = 1.378 (pyramidal) and 1.345 Å (planar) taken from the corresponding optimized PH_3 geometries (Table I).

of substituted aminophosphines. Several structural studies[15] of acyclic aminophosphines indicate that these compounds possess approximately trigonal planar geometry at nitrogen. Interestingly, the ground-state conformation of acyclic aminophosphines is isostructural with **2**, the "bisected" inversional transition state of A_2H_4 molecules.

The experimentally observable N–P torsional barriers of acyclic aminophosphines range from 8 to 10 kcal/mol,[4] although there are some examples of larger barriers for both cyclic[16] and acyclic[17] species. Ab initio MO calculations on H_2NPH_2 indicate that the ground-state geometry corresponds to **2**;[18] however, in the torsional transition state, **4**, the nitrogen

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geometry changes from trigonal planar to pyramidal.[19] The phosphorus pyramidal inversion barrier of H_2NPH_2 is computed to be larger than that of PH_3.[20]

The specific purposes of the present article are: (1) to examine the rotation–inversion behavior of N_2H_4, P_2H_4, and H_2NPH_2, utilizing ab initio MO methods; (2) to analyze the results of (1) by means of quantitative perturbational molecular orbital (PMO) theory;[21] (3) using PMO theory,[21] to investigate the factors responsible for the relative magnitudes of the pyramidal inversion barriers in A_2H_4 molecules (A = N, P) compared to those of simple AH_3 systems.

Computational Details

All computations were performed on the Burroughs B6700 computer of Queen's University, using a locally modified version of the GAUSSIAN 70 program system. A preliminary examination of the three molecules at the STO-3G and 4-31G levels with either standard or partially optimized geometrical parameters revealed that rotation in the ground states of diphosphine and aminophosphine was reasonably well reproduced at the STO-3G level. However, at this level of computation, the anti conformation of hydrazine was found to be more stable than the gauche ($\phi = 90°$) conformation, in disagreement with the experimental observations.[5] The same result was obtained when the geometries of the gauche and anti conformations of hydrazine were fully optimized by the FORCE method.[22] A proper ordering of the relative stabilities of the two conformations was achieved by recomputation of the energies at the 4-31G level using the STO-3G optimized geometries (i.e., 4-31G (STO-3G)). Since it was desired to provide the PMO analysis for all three molecules at a common computational level, all subsequent work was performed by the 4-31G (STO-3G) procedure. This decision in turn introduced an additional problem in the case of hydrazine, since it is well established[23] that pyramidal inversion barriers associated with first-row atoms are underestimated considerably at the 4-31G level. For example, the pyramidal inversion barrier computed for PH_3 in the present work by the 4-31G (STO-3G) method (33.41 kcal/mol; see Table I) agrees well both with a 4-31G (4-31G) calculation (34.61 kcal/mol) and also with calculations performed using other basis sets.[24] In the case of ammonia,[23] the 4-31G (STO-3G) method gives a negative inversion barrier. Consequently, a PMO analysis is unreasonable for the inversion process itself,[25] but rotation in the ground state **1**, a distinction between **2** and **3**, and substituent effects upon the inversion barriers remained accessible.

The program for the computation of orbital interactions is implemented by specification of a particular fragmentation mode following the SCF calculation at a particular geometry of interest; the fragment orbitals, and all of the properties of these orbitals required for the computation of orbital interactions, are then provided by the program. The two-orbital two-electron and two-orbital four-electron interaction energies are calculated using eq 1 and 2, respectively, where e_i^0 and e_j^0 are the energies of the fragment orbitals ϕ_i^0 and ϕ_j^0, and $\tilde{S}_{ij}$ and Δ_{ij} are the overlap integral and the interaction matrix element between the fragment orbitals, respectively.[21]

$$\Delta e_{ij} = 2(\Delta_{ij} - e_i^0\tilde{S}_{ij})^2/(e_i^0 - e_j^0) \qquad (1)$$

$$\Delta e_{ij} = 2\tilde{S}_{ij}[-2\Delta_{ij} + (e_i^0 + e_j^0)\tilde{S}_{ij}]/(1 - \tilde{S}_{ij}^2) \qquad (2)$$

Results and Discussion

A. Ab Initio Calculations. 1. P_2H_4. With one exception,[10b] previous calculations of the torsional process in P_2H_4 have indicated that the gauche conformation is the most stable. Wagner's study[10b] suggested that the anti conformation is insignificantly more stable than the gauche by ~0.1 kcal/mol. According to the present 4-31G (STO-3G) calculations, the energies of the gauche and anti conformations are essentially identical (Table II). The computed rotational potential function is rather flat in the 50–310° dihedral angle range as can be seen in Figure 1. This fact has been commented upon previously by Ahlrichs et al.[10d] Our computed gauche-anti energy difference of 0.232 kcal/mol is slightly lower than previous estimates; however, the gauche–syn energy difference of 3.16 kcal/mol is in reasonable accord with the values 4.02–4.85 which are available in the literature.[10d,e]

Pyramidal inversion in P_2H_4 may proceed via transition state **2** or transition state **3**.[26] Since the calculated energies of **2** and **3** are 30.44 and 36.55 kcal/mol, respectively, above that of the gauche conformation, which is the global minimum of the rotation–inversion surface, **2** is the transition state for pyramidal inversion in P_2H_4. It is noteworthy that this 30.44 kcal/mol barrier to pyramidal inversion in P_2H_4 is lower than the 33.4 kcal/mol barrier computed for PH_3 by the same procedure. This result is consistent with the experimental observations of Lambert and his co-workers.[13,27]

2. N_2H_4. In view of the previous extensive computations on N_2H_4,[6] and the problems noted under Computational Details, only the gauche (**1**, ϕ = 91.5°) and anti (**1**, ϕ = 180°)

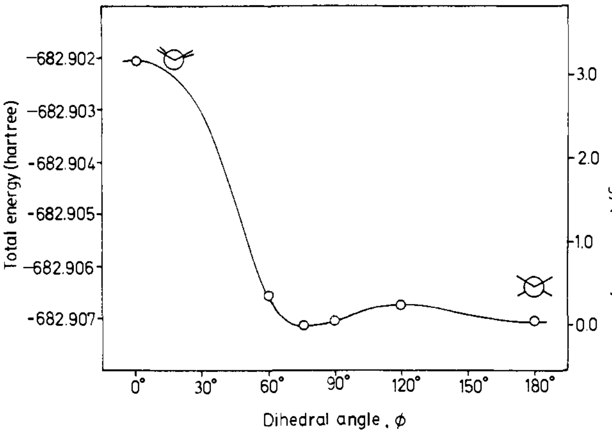


Figure 1. Rotational potential function for P_2H_4 computed by the 4-31G (STO-3G) procedure. Except for the P–H bond lengths (see text) each of the points shown in this figure corresponds to a fully optimized geometry at the STO-3G level.

Table III. Optimized Geometries and Total Energies Computed for N_2H_4 by the 4-31G (STO-3G) Method

conformation	r_{N-H}, Å	r_{N-N}, Å	∠HNH, deg	energy, au
1 ($\phi = 90°$)	1.032	1.471	105.61	−110.992 30[a]
1 ($\phi = 180°$)	1.032	1.472	103.37	−110.991 68[b]
2	1.036[c] 0.996[d]	1.423	105.45	−110.995 68
3	1.040[c] 0.992[d]	1.464	102.47	−110.977 39

[a] At the 4-31G* (STO-3G) level, the computed total energy is −111.054 98 au. [b] At the 4-31G* (STO-3G) level, the computed total energy is −111.054 46 au. [c] Refers to the pyramidal NH_2 group. [d] Refers to the planar NH_2 group.

ground-state geometries were investigated, together with conformations **2** and **3**. In each case the geometry was optimized fully, and the results are summarized in Table III.

The gauche conformation is calculated to be 0.40 kcal/mol more stable than the anti. As in the case of P_2H_4, conformation **2** is favored over conformation **3**, in this case by 11.48 kcal/mol. The same trend has been noted in another set of ab initio calculations[6f] in which it was found that the pyramidal inversion barrier computed for N_2H_4 (6.1 kcal/mol) is slightly higher than that computed for NH_3 (6.0 kcal/mol).

Taking into account all of the information now available,[6,10] it appears that the rotation-inversion behavior of N_2H_4 and P_2H_4 may be summarized as follows:

(1) Only the gauche conformation is a minimum on the rotational curve of N_2H_4.

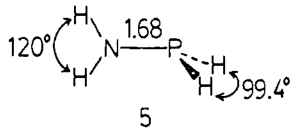
(2) The rotational curve of P_2H_4 possesses minima corresponding to both gauche and anti conformations.

(3) The pyramidal inversion barrier of P_2H_4 is significantly lower than that of PH_3.

(4) The pyramidal inversion barrier of N_2H_4 is slightly higher than that of NH_3.

(5) The "bisected" conformation, **2**, is the transition state for pyramidal inversion in both P_2H_4 and N_2H_4.

3. H_2NPH_2. In our earlier ab initio calculations on H_2NPH_2,[18-20] the POLYATOM program system was employed, because it was of interest to determine the effect of d-type functions upon the results. It was found, using a double ζ quality basis set containing two sets of d-type functions on phosphorus, one set of d-type functions on nitrogen, and one set of p-type functions on each of the four hydrogens, that the ground state of this molecule has structure **5**. The compound has the "bisected" geometry (ϕ = 90°) and an N–P bond length of 1.68 Å under the restrictions that ∠HPH = ∠HPN, ∠HNH = ∠HNP, and the N–H and P–H bond lengths are 1.02 and 1.42 Å, respectively. The geometry at nitrogen remains trigonal planar even when the polarization functions are removed. This result is consistent with several structure determinations,[15] and with dynamic NMR[4] and photoelectron spectroscopic measurements[28] on substituted aminophosphines.



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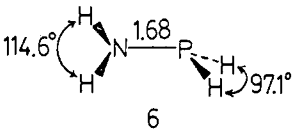

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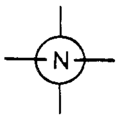
In a subsequent CNDO/2 calculation on H_2NPH_2, it has been found that the nitrogen geometry is slightly nonplanar.[29,30] It was suggested[29] that the difference between the CNDO/2 and POLYATOM calculations resulted from our restriction that ∠HNH = ∠HNP. To check this point, STO-3G calculations have now been performed on H_2NPH_2 with retention of the restriction that ∠HNH = ∠HNP. This has led to the geometry shown in **6**. Thus, as noted earlier,[23,32] the poorer quality STO-3G basis set tends to overemphasize nitrogen pyramidality regardless of the manner in which the HNH and HNP angles are treated. We believe that this comment also applies to the CNDO/2 calculations.[29] In any event, the salient point is that the NH_2 group is significantly more planar in H_2NPH_2 than in NH_3 or N_2H_4. For the PMO analyses of the present work, the 4-31G wave functions of conformations **2** and **4** of H_2NPH_2 were obtained, using the geometries of the earlier POLYATOM calculations. In addition, **7**, the transition state for pyramidal inversion at phosphorus, was examined, using the N–H, P–H, and N–P bond lengths of **2**. The resulting total energies follow: **2**, −396.976 40 au; **4**, −396.957 65 au; **7**, −396.915 15 au. Thus, at the 4-31G level, the rotational barrier in aminophosphine is calculated to be 11.77 kcal/mol, and the barrier to pyramidal inversion at phosphorus is calculated to be 38.45 kcal/mol, i.e., higher than that of PH_3, as observed earlier,[20] in the POLYATOM calculations.



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B. PMO Analyses. The PMO analysis of an A_2H_4 molecule consists of the fragmentation $H_2A\cdots AH_2$, and computation of the interaction energies associated with the orbitals of the AH_2 fragments that contribute to the highest occupied molecular orbital (HOMO) of the molecule.[21] The analysis of a molecule H_2ABH_2 proceeds via the fragmentation $H_2A\cdots BH_2$. For NH_2 and PH_2 fragments, the orbitals of interest are the nitrogen or phosphorus nonbonding electron pairs (n), the σ^* NH_2 and PH_2 orbitals, and the π and π^*-type NH_2 and PH_2 orbitals. For NH_2, σ^* is the lowest lying unoccupied orbital; for PH_2, π^* lies lower than σ^*. These are shown in Figure 2 for a general AH_2 or BH_2 fragment having pyramidal and planar configurations at the central atoms. As described elsewhere,[21,33] the computer program for the PMO analysis provides these fragment orbitals and their energies, together with the overlap integrals and matrix interaction elements between the fragments, and the electron occupancies of the fragments. The interaction energies are then calculated using eq 1 and 2.

The interaction diagram associated with the gauche ground-state conformation of A_2H_4 is shown in Figure 3. The (n-π) destabilizing interaction **8**, the (n-π^*) stabilizing interaction **9**, and the (n-σ^*) stabilizing interaction **10**, are

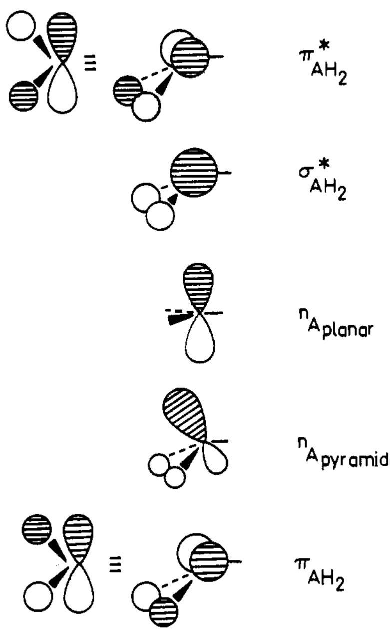
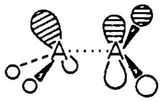


Figure 2. The orbitals of an AH_2 or BH_2 fragment which contribute to the HOMO of A_2H_4 or H_2ABH_2 molecules, and which are used in the PMO analysis.

shown below; **9** and **10,** are the molecular orbital counterparts of the hyperconjugative interaction shown in **11.** The difference between the two descriptions is that, although charge transfer is implied by both descriptions, **11** envisages an electron transfer from a lone pair to an adjacent A-H *bond,* whereas **9** and **10** describe orbital interactions with an AH_2 *group.*



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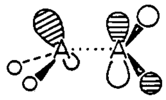

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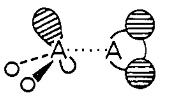

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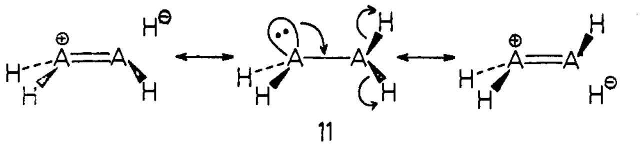

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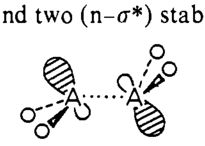
The corresponding interaction diagram for the anti conformation of A_2H_4 is shown in Figure 4. In this case, there is one (n-n) destabilizing interaction (**12**), one (π-π) destabilizing interaction (**13**), two (π-π^*) stabilizing interactions (**14**), and two (n-σ^*) stabilizing interactions (**15**).



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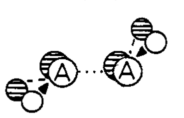

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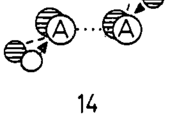

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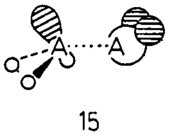

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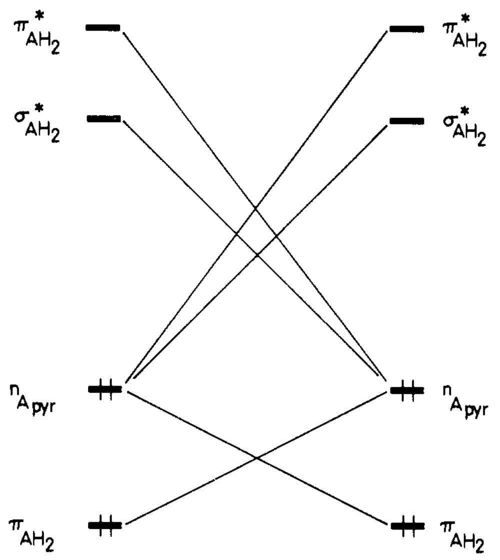


Figure 3. Interaction diagram for the PMO analysis of the gauche ground-state geometry of A_2H_4.

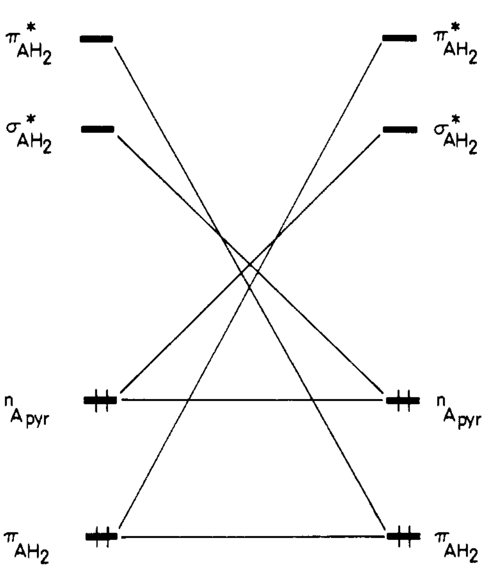


Figure 4. Interaction diagram for the PMO analysis of the anti ground-state geometry of A_2H_4.

The interaction diagrams for conformations corresponding to **2** and **3** are shown in Figures 5 and 6, respectively. The nonbonding n level lies higher in a planar AH_2 or BH_2 moiety, because there is no contribution from s orbitals. The π level of planar AH_2 or BH_2 lies lower, and the π^* level lies higher than in pyramidal AH_2 or BH_2, because the overlap between carbon 2p and hydrogen 1s orbitals is increased in the occupied orbital and is decreased in the unoccupied orbital as the HAH or HBH angle is increased. For similar reasons, the σ^* level is lower in planar AH_2 or BH_2 than in pyramidal AH_2 or BH_2. To illustrate these points, the energies of the fragment orbitals of conformation **2** of hydrazine have been included in Figure 5.

Table IV summarizes the quantitative PMO analyses of the 4-31G wave functions of the various conformations of N_2H_4, P_2H_4, and H_2NPH_2 examined in this work. In Table V, the same data are used to provide the stabilizing, destabilizing, and total PMO interaction energies in the three molecules.

N_2H_4 and P_2H_4. All stabilizing and destabilizing interaction energies are larger in N_2H_4 than in P_2H_4. This is especially significant when the (n-π^*) and (n-σ^*) stabilizing interactions are considered. The energy gap in these cases is smaller for phosphorus than for nitrogen, because n_P lies higher than n_N and $\pi^*_{PH_2}$ and $\sigma^*_{PH_2}$ lie lower than $\pi^*_{NH_2}$ and $\sigma^*_{NH_2}$. It is, therefore, clear that the differences between the two molecules are dominated by the larger overlap between fragments which exists at the shorter bond distance of hydrazine.

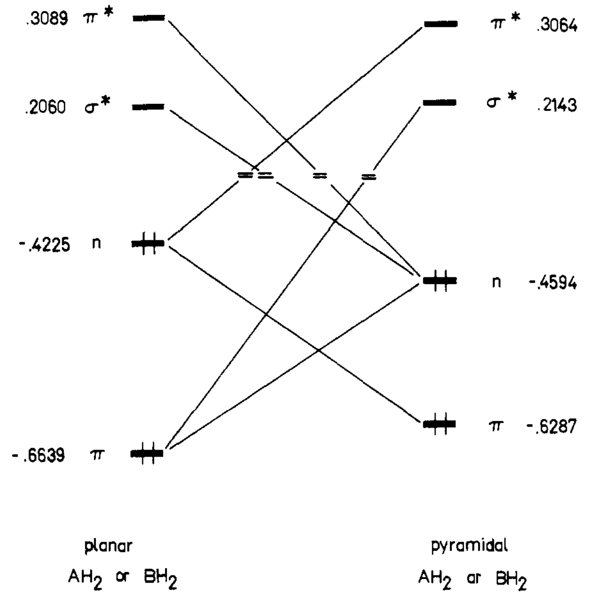


Figure 5. Interaction diagram for the PMO analysis of conformation **2** of an A_2H_4 or H_2ABH_2 molecule. The numbers refer to those computed for hydrazine at the 4-31G level.

Table IV. Quantitative PMO Analyses of Hydrazine, Diphosphine, and Aminophosphine

conformation	interaction	interaction energy, kcal/mol		
		N_2H_4	P_2H_4	H_2NPH_2
1 (ϕ = 91.5°)	$2(n-\pi)$	61.60		
	$2(n-\pi^*)$	−2.24		
	$2(n-\sigma^*)$	−3.68		
1 (ϕ = 90°)	$2(n-\pi)$		20.52	
	$2(n-\pi^*)$		−1.80	
	$2(n-\sigma^*)$		0.00	
1 (ϕ = 76°)	$2(n-\pi)$		19.06	
	$(\pi-\pi)$		0.29	
	$(n-n)$		0.30	
	$2(n-\pi^*)$		−1.66	
	$2(\pi-\pi^*)$		−0.16	
	$2(n-\sigma^*)$		−0.08	
1 (ϕ = 180°)	$(n-n)$	46.04	15.84	
	$(\pi-\pi)$	26.09	7.21	
	$2(n-\sigma^*)$	−1.56	−0.40	
	$2(\pi-\pi^*)$	−2.46	−1.06	
2	$(n_{pln}-\pi_{pyr})$	46.61	20.12	27.32[a]
	$(n_{pyr}-\pi_{pln})$	26.94	6.58	22.58
	$(n_{pln}-\pi^*_{pyr})$	−2.26	−3.26	−4.34
	$(n_{pyr}-\pi^*_{pln})$	−1.24	−2.62	−0.68
	$(n_{pln}-\sigma^*_{pyr})$	0.00	0.00	0.00
	$(n_{pyr}-\sigma^*_{pln})$	−5.96	−0.57	−3.85
3	$(n_{pln}-n_{pyr})$	45.84	21.93	
	$(\pi_{pln}-\pi_{pyr})$	22.47	5.67	
	$(\pi_{pln}-\pi^*_{pyr})$	−0.44	−0.04	
	$(\pi_{pyr}-\pi^*_{pln})$	−0.99	−0.67	
	$(n_{pln}-\sigma^*_{pyr})$	−0.13	−0.78	
	$(n_{pyr}-\sigma^*_{pln})$	−0.41	−0.36	
4	$(n-n)$			40.24
	$(\pi-\pi)$			17.42
	$2(n-\sigma^*)$			−2.26[b]
	$2(\pi-\pi^*)$			−1.73[c]
7	$(n_N-\pi_{PH_2})$			19.36
	$(n_P-\pi_{NH_2})$			35.36
	$(n_N-\pi^*_{PH_2})$			−6.39
	$(n_P-\pi^*_{NH_2})$			−1.69

[a] For aminophosphine, the subscripts pyr (pyramidal) and pln (planar) refer to phosphorus and nitrogen, respectively. [b] This is the sum of $(n_P-\sigma^*_{NH_2})$ (−1.04 kcal/mol) and $(n_N-\sigma^*_{PH_2})$ (−1.22 kcal/mol). [c] This is the sum of $(\pi_{PH_2}-\pi^*_{NH_2})$ (−0.61 kcal/mol) and $(\pi_{NH_2}-\pi^*_{PH_2})$ (−1.12 kcal/mol).

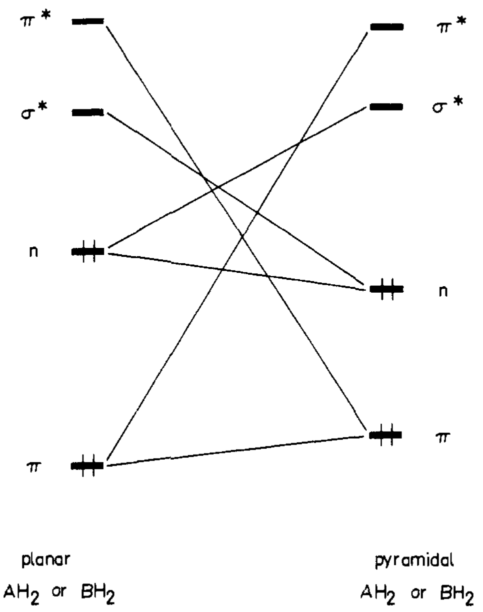


Figure 6. Interaction diagram for the PMO analysis of conformation **3** of an A_2H_4 or H_2ABH_2 molecule.

In both molecules, the gauche conformation is more stabilized, and less destabilized, than the anti conformation. Since the same trends were observed in the PMO analyses of the staggered and eclipsed conformations of ethane,[21] it might be concluded that there is no fundamental difference between the conformational behavior of these A_2H_4 molecules, containing adjacent electron pairs, and that of A_2H_6 molecules. Indeed, this is the interpretation given by Mislow and his co-workers[34] to the finding that tetraalkyldisilanes and tetraalkyldiphosphines exhibit similar static and dynamic stereochemical behavior. These workers therefore argue that there is no compelling need to invoke special electronic effects, e.g., the "gauche effect",[35] to account for the conformational preferences of tetraalkyldiphosphines, which, instead, are "*primarily* dictated by the same steric factors as in the corresponding disilanes".

The arguments employed by Mislow and his co-workers are inappropriate for us because molecular orbital calculations do not provide a rigorous definition of "steric factors", as we have pointed our recently.[36] However, it must be noted that, although the relative stabilities of the gauche conformations of N_2H_4 and P_2H_4 have been reproduced, the PMO analysis has greatly overestimated the gauche preference in both cases.[37] Thus, in its present form, the PMO method would have to be regarded as incomplete.

In their work on the Fourier component analysis of internal rotation in saturated molecules, Radom, Hehre, and Pople[6e] have proposed an interpretation of a rotational potential function in terms of onefold (V_1), twofold (V_2), and threefold (V_3) Fourier components. The V_2 term is interpreted by these workers as an orbital interaction term, and it may be positive or negative, depending on whether stabilizing or destabilizing mechanisms, respectively, are dominant. This interpretation suggests that the V_2 term of a Fourier component analysis should correspond to our PMO interaction energies. It is interesting that the Fourier component analysis of hydrazine (shown in Figure 3b of ref 6e) indicates that V_2 favors the gauche conformation over the anti by 7.92 kcal/mol. The total energy difference is reduced by the V_1 term of the Fourier component analysis, which favors the anti conformation by 7.42 kcal/mol, and is interpreted in terms of dipole-dipole interactions between the lone pairs, such interactions being minimized in the anti conformation. The nonzero V_1 term may,

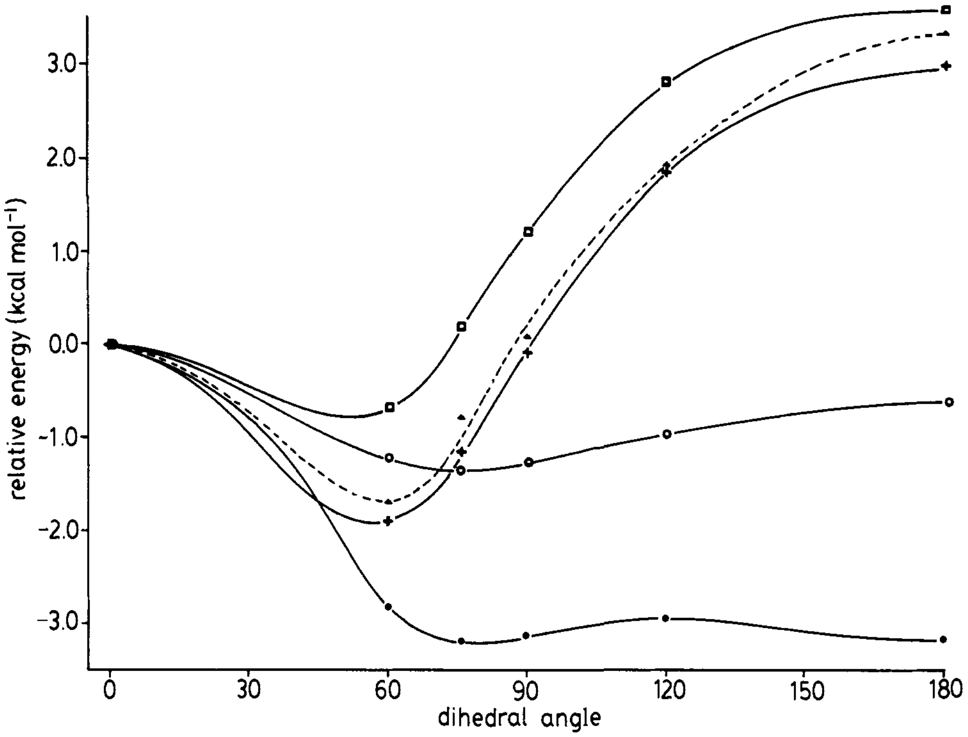


Figure 7. The computed rotational potential of P_2H_4 at the 4-31G level (—●—), together with the two-electron stabilizing interactions (—○—), the four-electron destabilizing interactions (—□—), the total PMO interaction term (—+—), and $\epsilon_{HOMO}/4.66$ (—▲—) associated with this rotational potential.

Table V. Stabilizing, Destabilizing, and Total PMO Interaction Energies in Hydrazine, Diphosphine, and Aminophosphine

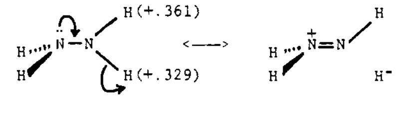
	interaction energy, kcal/mol								
	stabilizing			destabilizing			total		
conformation	N_2H_4	P_2H_4	NH_2PH_2	N_2H_4	P_2H_4	NH_2PH_2	N_2H_4	P_2H_4	NH_2PH_2
1 (ϕ = 90°)	−5.92 (−6.50)[a,b]	−1.80 (−2.57)		61.60 (43.78)[b]	20.52 (11.50)		55.68 (37.28)[b]	18.72 (8.93)	
1 (ϕ = 76°)		−1.90			19.06			17.16	
1 (ϕ = 180°)	−4.02 (−4.07)	−1.46 (−2.47)		72.13 (44.69)	23.05 (10.77)		68.11 (40.62)	21.59 (8.30)	
2	−9.46 (−8.82)	−6.45	−8.87 (−12.06)	73.55 (51.22)	26.70	49.90 (30.00)	64.09 (42.40)	20.25	41.03 (17.94)
3	−2.97 (−2.01)	−1.85		68.31 (44.64)	27.60		65.34 (42.63)	25.75	
4			−3.99 (−6.72)			57.66 (31.89)			53.67 (25.17)
7			−8.08 (−17.55)			54.72 (33.23)			46.64 (15.68)

[a] Numbers in parentheses were obtained at the STO-3G (STO-3G) level. [b] At the 4-31G* (STO-3G) level, the stabilizing, destabilizing, and total interaction energies computed for N_2H_4 are −5.07, 68.06, and 62.46 kcal/mol for the 90° conformation and −3.18, 74.25, and 71.07 kcal/mol for the 180° conformation.

therefore, reflect the noncancellation of V_{ee} and V_{nn} discussed in footnote 37. However, the PMO analysis is still needed, because it provides a rather simple rationalization of why the conformation is gauche and not anti.

Turning to the PMO analysis itself, the data of Table V indicate that the gauche preferences of N_2H_4 and P_2H_4 are primarily caused by a "minimization of repulsive forces" in both cases.

On the other hand, the preference for the bisected inversional transition state **2** over **3** is primarily the result of a "maximization of attractive forces".[45] For N_2H_4, the largest contributor to this stabilization is the "hyperconjugative interaction" **16**, in which the pyramidal "lone pair" and an adjacent NH bond are antiperiplanar. The atomic charges shown in **16** should be noted. The stabilizing mechanism is different for P_2H_4. The largest contributors are now the (n-π^*) interactions associated with both lone pairs.



16

The double energy difference $[(E_1^{A_2H_4} - E_2^{A_2H_4}) - (E_{pyr}^{AH_3} - E_{plan}^{AH_3})]$, where E_i is the relevant total interaction energy, gives in PMO terms the effect on the inversion barrier of the replacement of a hydrogen of AH_3 by the group AH_2. The second term in this expansion is small, because of the absence of π-type orbital interactions in AH_3. The appropriate E_1 for N_2H_4 refers to the gauche conformation, and that for P_2H_4 refers to the anti conformation, because this leads to the lowest energy difference between the ground state and the inversional transition state.

Using the data of Table V, this PMO analysis of substituent

Table VI. Energies of the NH_2 and PH_2 Fragment Orbitals of Conformation **2** of H_2NPH_2

orbital	energy, au	orbital	energy, au
$\pi^*_{NH_2}$	0.2989	n_N	−0.4254
$\sigma^*_{PH_2}$	0.1900	π_{PH_2}	−0.5229
$\sigma^*_{NH_2}$	0.1833	π_{NH_2}	−0.6226
n_P	−0.3817		

effects predicts that N_2H_4 should have a *higher* inversion barrier than NH_3 by 8.41 kcal/mol, and that P_2H_4 should have a *lower* inversion barrier than PH_3 by 1.34 kcal/mol. In both A_2H_4 molecules, the inversional transition state **2** has greater stabilization and also greater destabilization than the ground state **1**. However, in N_2H_4 the destabilization in **2** dominates, leading to the higher barrier than NH_3; and in P_2H_4 the stabilization in **2** dominates, leading to the lower barrier than PH_3.

A final point of interest is that the quantitative PMO analysis provides insight into the factors responsible for the lower energy of **1** ($\phi = 76°$) than **1** ($\phi = 90°$) in P_2H_4. As the dihedral angle is decreased from 90°, the ($n-\pi$) and ($n-\pi^*$) interactions decrease, because the overlap between the fragments decreases. At the same time, contributions appear from (n−n), ($\pi-\pi$), and ($\pi-\pi^*$). This can be seen in Table V. According to these data, the decreased *destabilization* associated with the decreased ($n-\pi$) interaction is not quite compensated by the appearance of (n−n) and ($\pi-\pi$), and this is mainly responsible for the nonorthogonal geometry. In contrast, N_2H_4 prefers a near-90° dihedral angle because in this case the (n−n) destabilizing interaction, which appears when the molecule is rotated away from 90°, is the largest single contributor to the interaction energy. These views are consistent with the conclusion already reached, that the ground states of N_2H_4 and P_2H_4 are best understood in terms of a minimization of repulsive forces.[45]

H_2NPH_2. The difference in the total interaction energies of **2** and **4**, shown in Table V (12.64 kcal/mol), compares favorably with the calculated total energy difference of 11.77 kcal/mol. The PMO energy difference provides the rotational barrier of the molecule; it also accounts for the effect on the pyramidal inversion barrier associated with the replacement of a hydrogen of NH_3 by a PH_2 group, viz., a substantial decrease. The difference in the total interaction energies of **2** and **7** corresponds to the effect on the pyramidal inversion barrier of PH_3 caused by the replacement of one hydrogen by an NH_2 group. The increase is 5.61 kcal/mol, which again compares favorably with the 5.05 kcal/mol increase in the barrier provided by the total energies. Thus the quantitative PMO analysis of H_2NPH_2 is in almost quantitative agreement with the static and dynamic stereochemistry that is obtained for this molecule in the total energy calculations.

Examination of the *stabilizing* interactions in **2** reveals a net charge transfer *from phosphorus to nitrogen*, because ($n_P - \sigma^*_{NH_2}$) + ($n_P - \pi^*_{NH_2}$) is larger numerically than ($n_N - \sigma^*_{PH_2}$) + ($n_N - \pi^*_{PH_2}$). This is consistent with our earlier observation,[18] based upon a Mulliken population analysis. However, as already noted, it is the *destabilizing* interactions which are mainly responsible for the conformational preference of H_2NPH_2. This means that our heuristic interpretation of the lower nitrogen inversion barrier and the higher phosphorus inversion barrier in terms of electron release from PH_2 to NH_2[18] and electron withdrawal by NH_2 from PH_2[20] is not supported by the PMO analysis. Nevertheless, relationships between ligand electronegativity and the magnitudes of pyramidal inversion barriers[46] are quite compatible with the present work, although not in the manner that we had supposed. Electronegativity effects enter into the PMO analysis in the different energies of NH_2 and PH_2 group orbitals. Except for σ^*, all of the occupied PH_2 orbitals lie higher, and all of the unoccupied PH_2 orbitals lie lower, than those of NH_2. This is shown in Table VI, which lists the energies of the NH_2 and PH_2 fragment orbitals of conformation **2**.

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(37) In Hartree–Fock SCF theory, the total energy, E_T, of a closed-shell system is given by $E_T = (2\sum_k \epsilon_k - V_{ee} + V_{nn})$, where the ϵ_k's are the canonical orbital energies, V_{ee} is the electron–electron repulsion energy, and V_{nn} is the nuclear–nuclear repulsion energy.[38] We now speculate that the earlier successes of the PMO method of conformational analysis, when applied to hydrocarbon molecules,[39] were the result of a fortuitous conformational invariance of $(-V_{ee} + V_{nn})$.[40,41]

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(41) It is useful to comment at this point on the relevance, to a PMO interpretation, of the observation[42] that $E_T^{SCF} = K\Sigma_i^{occ} 2\epsilon_i$, since this relationship is obeyed by the molecules of the present investigation. At the 4-31G level, K is found to be 1.54, 1.62, and 1.61 for hydrazine, diphosphine, and aminophosphine, respectively, and to be conformationally invariant. At the STO-3G level, hydrazine is found to have $K = 1.56$. According to one of the referees, a quantitative PMO analysis within a SCF scheme would have no meaning, unless the above relationship can be shown to exist, with K identical not only for the different molecules, but also for the fragments and the molecule. In our view, if the validity of the PMO analysis were to be dependent upon the existence of a Ruedenberg relationship,[42a] it would become necessary to treat *all possible* orbital interactions between the fragments. The method would thereby be reduced to a problem of bookkeeping, with loss of the (hoped-for) simple picture. To avoid this problem, we assume that the conformational behavior of a molecule is paralleled by the behavior of the HOMO.[43] When this assumption is valid, an understanding of the behavior of the HOMO provides some understanding of the behavior of the molecule. The mathematical formalism presented in ref 21 permits a transformation of the computed molecular orbitals from an atomic orbital basis to a fragment orbital basis. For each conformation, the HOMO is then reconstructed in terms of the fragment orbital interactions that contribute to that HOMO. With this formalism, the first-order term of the perturbational expansion is included in the fragment orbital energy, and the form of the HOMO is then reproduced by the second-order term calculated with eq 1 and 2. Figure 7 illustrates the application of this operational procedure to the rotational potential of diphosphine shown in Figure 1. The various curves in Figure 7 refer to E_T, the two-electron contribution to the HOMO, the four-electron contribution to the HOMO, the total PMO contribution to the HOMO, and ϵ_{HOMO}. The curve for ϵ_{HOMO} has been multiplied by a constant factor of 1/4.66, i.e., $\Sigma\Delta e_{ij} \simeq K'\epsilon_{HOMO}$. Although the two-electron PMO term most closely resembles E_T in the present case, we have no evidence that such behavior will be observed generally. To overcome the charge that the PMO analysis is arbitrary, we therefore advocate that this analysis be based upon the HOMO.[44]

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(44) A PMO analysis of rotation in hydrazine based upon "tempered" orbitals[38] predicts the anti conformation of hydrazine to be ca. 30 kcal less stable than the gauche.

(45) A referee has pointed out that such conclusions are basis set dependent, and has urged caution in this regard. We comment that, in terms of our operational procedure, described in footnote 41, a basis set that reproduces an experimental trend should also produce a reliable PMO analysis. To check this point, we repeated the quantitative PMO analysis on the three molecules at the STO-3G (STO-3G) level, with the results shown in parentheses in Table V. It is clear that the *stabilizing interactions* dominate at the STO-3G level. It is also clear that the PMO analysis at this computational level has failed. The 90° conformation is predicted to be more stable in the case of hydrazine, and the 180° conformation is predicted to be more stable in the case of diphosphine. The total energy behavior is just the opposite in both cases. A final calculation was then performed on the 90 and 180° conformations of hydrazine at the 4-31G* (STO-3G) level. The results of these calculations, summarized in footnotes a and b of Table III and footnote b of Table V, indicate that the 4-31G and 4-31G* basis sets lead to the same conclusions concerning both the total energy and the PMO behavior. We therefore suggest that the procedures advocated herein contain proper safeguards concerning the relative importance of stabilizing and destabilizing interactions. We also suggest that much more work will be needed before reliable qualitative rules can be provided for the PMO analysis of molecules containing adjacent electron pairs.

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Formation of Stable Monolayer Membranes and Related Structures in Dilute Aqueous Solution from Two-Headed Ammonium Amphiphiles

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Abstract: Two-headed, single-chain ammonium amphiphiles in which the hydrophobic chain was made of the flexible decamethylene unit and the rigid diphenylazomethine or biphenyl unit were synthesized. These amphiphiles produced huge (10^6–10^7 daltons) aggregates in dilute aqueous solution. The basic structure of the aggregates was shown by electron microscopy to be the monolayer membrane. A rod-like structure resulted, when the flexible moiety increased. Addition of second components drastically changed the aggregate structure. For instance, rigid lamellae were converted to large single-walled vesicles by incorporation of cholesterol. The present finding is the first example of the formation of stable monolayer membranes.

Stable bilayer membranes have been prepared in dilute aqueous solution from a variety of totally synthetic amphiphiles which contain two higher alkyl chains (C_{10}–C_{18}) as the hydrophobic moiety. The hydrophilic group of these amphiphiles may be cationic,[1-5] anionic,[6,7] nonionic,[8] or zwitterionic.[8] In very recent studies, it is shown that the hydrophobic portion of these bilayer-forming amphiphiles can be replaced by a single-chain unit which contains a rigid segment such as diphenylazomethine[9] or biphenyl group.[10] Figures 1a,b illustrates schematically these bilayer structures.

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