Theoretical Prediction of Vibrational Spectra. 2. Force Field, Spectroscopically Refined Geometry, and Reassignment of the Vibrational Spectrum of Naphthalene[1]

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Abstract: The complete harmonic force field of naphthalene has been calculated ab initio at the 4-21 Hartree–Fock level. The diagonal force constants were then scaled with the scale factors previously derived by fitting the similarly computed vibrational spectrum of benzene to its observed spectrum. The resulting SQM (naphthalene 4-21/benzene) force field was used to compute the vibrational spectra of the $C_{10}H_8$ and $C_{10}D_8$ forms of naphthalene. It was then possible to confirm some previously suggested reassignments of fundamental frequencies and to offer strong evidence for a few additional reassignments. The final comparison showed an average difference of only 6.5 cm^{-1} between the theoretical spectrum which had been predicted a priori, without benefit of any measurements on naphthalene, and the corrected experimental spectra. This comparison does not include the C–H stretch fundamentals which cannot be clearly assigned either on the basis of the experimental evidence or the combined experimental and theoretical data. The infrared absorption intensities have been calculated with an accuracy that is at least adequate for distinguishing qualitatively between strong, medium, and weak bands, and which is highly useful in the investigation of questionable assignments. Examination of the structural dependence of several band frequencies that are highly dependent on the relative length of the various C–C bonds in naphthalene lends strong support for the shortest bond length being in the region of $r_e = 1.372$ to 1.374 Å, rather than the longer value than has been favored by some authors. The highly accurate prediction a priori of the spectrum of naphthalene, coupled with similar results reported earlier for pyridine, indicates that ab initio computations at a modest level with transfer of scale constants from related molecules can be a widely applicable tool for the reliable prediction of infrared spectra of unknown molecules.

The widespread practical analytical application of infrared spectroscopy is based almost entirely on what is really very limited transferability of group frequencies between related molecules. For example, the characteristic narrow frequency region in which carbonyl or S–H frequencies are expected to fall provides a ready structural identification of these groups. It has been hoped for a long time that a more wide-ranging correlation of molecular vibrational behavior could be obtained by looking at the more fundamental information contained in force constants, anticipating that these might have more general transferability when expressed in valence coordinates. This program has met with considerable success in the case of simple aliphatic hydrocarbons, but difficulties have arisen in applications to complex and strongly coupled systems.

The principal problem is the almost insuperable difficulty in obtaining the complete force field from experimental data, even in the harmonic approximation, for anything but the simplest molecules. There is hardly ever enough experimental information, unclouded by uncertainties of assignment, to obtain all of the coupling constants or even to show experimentally which ones are of negligible importance. An alternative is to calculate the complete force field by ab initio gradient techniques, a procedure which is now possible for molecules of reasonable size using moderate-sized basis sets at the Hartree–Fock level. Unfortunately, experience has shown that such calculations are in error by an unacceptable 10–20% and occasionally even more.

The observation that the error in computed force constants is quite systematic for a given basis set has led to the suggestion that scale factors be used to correct for this error. The simplest possibility would be to reduce all of the computed constants by 10 to 20%. Further examination suggests, however, that somewhat different factors should be employed for different types of vibrational motions.[2,3] Among the approaches suggested by various workers,[3–6] we prefer that illustrated in the study of benzene by Pulay et al.[6] using six scale factors in set II, ranging between 0.739 and 0.911 for the diagonal constants. Scale factors for the large number of coupling constants were not independently adjusted

but were taken as the geometric mean of those for the corresponding diagonal factors. An exception was made for the CC–CC couplings which were described by two separate scale factors, and for a CC ring deformation coupling. The values of the nine scale factors were determined by a least-squares fitting of the scaled fundamental frequencies to observed vibrational spectra of benzene and two of its deuterated forms. The resulting force field is believed to be the best available harmonic force field for benzene.

Beyond attempts to transfer vibrational group frequencies or force constant matrix elements between molecules, a third and deeper level of transferability is the transfer of scale factors. These represent the error, at some chosen level of theory, in the calculation of the force constants, and so would be expected to have greater transferability than the constants themselves. Such a procedure has been reported in a study of the force field of pyridine.[1] The harmonic force constant matrix of pyridine was calculated ab initio at the same level of theory as previously used for benzene. The scale factors for benzene were then used unchanged to derive what may be called a SQM (scaled quantum mechanical) (pyridine 4-21/benzene) force field for pyridine.[7] Vibrational spectra for pyridine and its deuterated derivatives predicted by this force field showed a mean deviation of only 5.7 cm^{-1} in all frequencies other than C–H stretches from experimental measurements. Including the C–H stretches, the mean deviation was 9.6 cm^{-1}. A common set of scale factors for simple organic π systems has been determined recently and the method was described in detail.[6]

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While the scaling procedure appears to correct very successfully for most of the systematic errors in computed ab initio force constants (basis set truncation, neglect of electron correlation, and some anharmonic influences), it obviously cannot correct for certain molecular effect such as large Fermi resonances. Nevertheless, if the scale factors do prove to be relatively transferable, the easy computation of highly accurate force constant matrices, and hence infrared and Raman spectra, of medium-sized molecules will become a practical reality.

It is not yet known how closely related molecules must be to permit accurate a priori calculation of vibrational spectra by transfer of scale factors.[9] In the present study, we investigate the question of whether the scale factors derived for benzene can be used to provide accurate spectral predictions for naphthalene in spite of the variety of inter-ring couplings present in the latter molecule which have no counterpart in benzene.

A test of the transferability of the scale factors from benzene to naphthalene requires comparison of the final computed vibrational spectrum of naphthalene with accurate experimental data. In spite of the wealth of experimental[10-32] and theoretical[33-41]

(9) Our method is not a truly *ab initio* calculation of a spectrum since it makes use of experimental information on a related molecule. It may be called *a priori*, however, since it is made in advance of any experiment (or reference to any existing experiment) on the substance under investigation.

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Table I. Internal Coordinates of Naphthalene[a]

$$\beta_1 = 2^{-1/2}(\phi_1 - \phi_2); \quad \beta_5 = 2^{-1/2}(\phi_9 - \phi_{10})$$
$$\beta_2 = 2^{-1/2}(\phi_3 - \phi_4)$$
$$\delta_4 = 6^{-1/2}(\alpha_7 - \alpha_8 + \alpha_9 - \alpha_{10} + \alpha_{11} - \alpha_{12})$$
$$\delta_5 = 12^{-1/2}(2\alpha_8 + 2\alpha_{11} - \alpha_9 - \alpha_{10} - \alpha_7 - \alpha_{12})$$
$$\delta_6 = 2^{-1}(\alpha_9 - \alpha_{10} + \alpha_{12} - \alpha_7)$$
$$\sigma_1 = 6^{-1/2}(\tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6)$$
$$\sigma_2 = 2^{-1}(\tau_2 - \tau_4 + \tau_5 - \tau_1)$$
$$\sigma_3 = 12^{-1/2}(2\tau_3 + 2\tau_6 - \tau_1 - \tau_2 - \tau_4 - \tau_5)$$
$$\Omega = 2^{-1/2}(\tau_{abcd} - \tau_{ebcf})$$

[a] δ_1 is analogous to δ_4, δ_2 to δ_5, etc.; similarly, σ_4 is analogous to σ_1. The γ's are the Wilson, Decius, and Cross wagging coordinates. The positive direction of $\gamma_1 - \gamma_4$ is out of the yz plane and the positive direction of $\gamma_5 - \gamma_8$ is into the yz plane. See Figure 1.
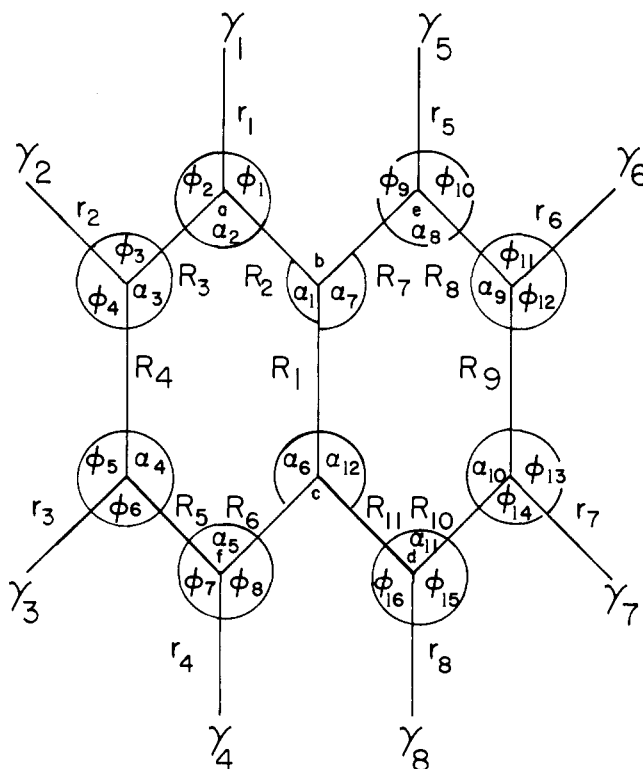

Figure 1. Labeling of coordinates in naphthalene.

studies of the vibrational spectrum of naphthalene, some questions still remain, as is common in analyses of vibrational spectra of molecules of this size. Polarized Raman spectra[23,24] and gas-phase infrared band contours[10-12,15,16] have been used to determine the symmetry of observed bands having sufficient intensity, but assignment of bands as fundamentals was often made on the basis of intensity alone. Several workers, notably Krainov,[33] Freeman and Ross,[34] Scully and Whiffen,[35] and Neto et al.,[36] sought to make assignments with the aid of normal coordinate analysis by the least-squares fitting of a limited number of force field parameters to a subset of the more confidently assigned frequencies. While giving an essentially correct picture of the normal vibrations of naphthalene, such empirical normal coordinate analyses cannot make conclusive decisions about doubtful assignments for such a complicated molecule without a great deal more experimental data than are currently available.

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The question of correct assignment of the vibrational funda-
mentals is a vital one for any consideration of the accuracy of
computed spectra. The larger number of plausible alternative
assignments in larger systems increases the risk of error when force
fields are based solely on experimental data. For example, in
Ohno's recent work[37] the B_{1u} mode at 810 cm^{-1} was taken as a
fundamental. However, Rich and Dows[32] demonstrated earlier
that this band disappears at low temperatures.

As a further experimental uncertainty, some details in the
structure of naphthalene are still under debate.[42-45] A recent gas
electron diffraction study[45] yielded an r_a value of 1.381 ± 0.002
Å for the length of the short CC bond, which is at odds with an
earlier electron diffraction result[42] and a corrected ab initio result[44]
of 1.371 Å. Values of 1.364 and 1.377 Å have been reported for
the length of this bond in the solid state from X-ray diffraction
experiments.[43,46] Several of the vibrations of naphthalene are
sensitive to the length of this bond, so that the present vibrational
analysis enables us now to add more information about the value
of this structural parameter.

We have employed a split valence 4-21 basis set[47] in the present
ab initio calculation of the force field of naphthalene so that the
set II scale factors of benzene[6] which were derived using the same
basis set could be directly adopted. It must be emphasized that
we have not fitted any scale factors to the spectra of naphthalene
in the present study; the scale factors we have used are those which
have been carried over unchanged from the benzene analysis. This
procedure gives us a strict test of the accuracy which can be
obtained by the transfer of such scale factors between related
molecules.

Calculations

The force and interaction constants of naphthalene were evaluated by
numerical differentiation of analytically determined first derivatives of
the energy with respect to nuclear displacement.[48] The computations
made use of the ab initio gradient program TEXAS[49] and the 4-21 basis
set[47] which has been thoroughly tested for the evaluation of molecular
geometries and vibrational force fields. Cartesian displacements of 0.005
Å were used in order that advantage could be taken of the partial sym-
metry of distorted geometries. Calculations at 24 unique distorted ge-
ometries were required to determine the Cartesian force constant matrix
by central difference numerical differentiation of the forces. The integral
neglect threshold and the convergence of the two electron energy were
both set at 10^{-7} to assure numerical accuracy.

The Cartesian force constant matrix and dipole moment derivatives
were transformed to the internal coordinate space defined in Table I and
Figure 1. We followed the recommendation of Pulay et al.[47] in our
choice of internal coordinates so that comparisons of the naphthalene
force field could be made with that of benzene and with related aromatic
systems. Normal coordinate calculations were carried out using Wilson's
FG matrix formalism.

Force Field of Naphthalene

The scaled quantum mechanical force field of naphthalene is
shown in Tables IIa and IIb. The directly computed force and
interaction constants have been scaled by the scale factors which
were previously optimized for benzene,[6] as indicated in the footnote
to Table IIa. The force field was evaluated at the spectroscopically
refined equilibrium geometry of naphthalene, obtained as discussed
below.

To permit some interesting comparisons, Table IIa separates
out the computed ring CC stretching constants and CC–CC in-
teraction constants and also shows a number of other attempts

to evaluate these quantities. Table IIa also shows the scaled
CNDO/2 force field of Grofcsik et al.[38] This force field was fitted
to the observed vibrational spectrum of naphthalene. In spite of
a similar scaling technique, there is a fundamental difference
between these two approaches: our force field is completely a priori
in the sence that no knowledge of the experimental spectrum is
assumed except to minor corrections to the geometry which are
discussed below.

Table IIa also shows two force fields obtained by Neto et al.[36]
and by Ohno[37] by simple fitting to experimental spectral data.
Some analogous force constants of benzene[6] are also shown for
comparison. A number of such empirical force fields for condensed
ring aromatics[34-37,41] give a simplified but qualitatively correct
description of the normal vibrations of naphthalene. The individual
force constants cannot always be considered very physical since
insufficient experimental information is available to determine
the complete force field, even in the harmonic approximation.
Furthermore, a number of the spectroscopic assignments that have
been made for naphthalene and which were used in obtaining the
empirical force fields are probably incorrect, as discussed more
fully below. Consequently, the empirically derived force fields
for naphthalene must be regarded only as parameters that have
been adjusted to fit a set of observed frequencies, some of which
may be incorrectly assigned as fundamentals. For example, both
the force fields of Net et al.[36] and that of Ohno[37] yield frequencies
in good agreement with their chosen observed frequencies despite
having values of coupling constants (for example, R_1R_3 and R_2R_6)
that are in serious disagreement with each other.

The correct algebraic sign of the CC–CC interaction constants
can be predicted from elementary considerations. If R_j expands
with shrinking R_k, then the interaction constant must be positive.
Similarly, if R_j and R_k simultaneously expand or shrink, then the
interaction constant must be negative. Hence, as read from a
resonance structure, like-bond interactions (single–single or
double–double) are negative and unlike-bond interactions are
positive. The resonance-preferred albegraic sign can thus be
obtained by considering all the possible rsonance structures with
equal weight. A perusal of Table IIa shows that the CC–CC
coupling constants calculated here are all in agreement with this
criterion.

The force fields of Neto et al.[36] and of Ohno[37] given in Table
IIa have been transformed from their original coordinate systems
to ours so that the results can be directly compared. It is not
possible to reconstruct the force field of Ohno directly from his
reported data.[37] For his Method II he employs bond orders from
Hückel calculations, which he does not give, although these bond
orders affect only the diagonal CC force constants. In an ap-
proximate reconstruction of his force field, we used bond orders
predicted by resonance theory (1.33333 and 1.66666 for naph-
thalene and 1.5 for benzene). The regenerated force field was
then transformed to our coordinate system, using a transformation
program briefly described in ref 50 and to be described more fully
in a manuscript in preparation.[51] The transformed force field
was then diagonalized, and frequencies were obtained which are
in good, although not perfect, agreement with Ohno's Method II
frequencies (see Table VIII of his paper). Aside from differences
in bond orders, contributions to these small deviations undoubtedly
arise from differences in the geometries used.

Table IIa shows that six of Ohno's CC–CC coupling constants
disagree in sign with ours and with those predicted by resonance.
The coupling constants of Neto et al. disagree in only one case,
and that constant is quite small. This comparison serves as a very
good illustration of the fact that empirically derived force fields
can be seriously in error in the value of individual elements of the
force matrix and still produce good agreement with the experi-
mental frequencies from which they were derived.

The consensus existing between the scaled ab initio and the
scaled CNDO/2 force fields is striking, being particularly good
in the CC–CC interaction space shown in Table IIa. In cases

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Table II

(a) Force Field of Naphthalene[a]

	this work	CNDO/2	ref 37[b]	ref 36	benzene
$R_1^2/2$	5.758	6.162	6.580	6.023	6.578
$R_2^2/2$	5.812	5.846	5.821	5.975	
$R_3^2/2$	7.379	7.268	7.379	7.051	
$R_4^2/2$	5.976	5.812	5.782	5.981	
R_1R_2	0.530	0.508	0.677	0.636	0.710
R_1R_3	-0.217	-0.160	0.297	-0.211	-0.407
R_1R_4	0.159	0.193	-0.286	0.066	0.425
R_2R_3	0.611	0.692	0.407	0.745	0.710
R_2R_4	-0.431	-0.327	-0.261	-0.318	-0.407
R_2R_5	0.271	0.278	-0.051	0.251	0.425
R_2R_6	-0.322	-0.295	0.262	-0.207	-0.407
R_2R_7	0.539	0.516	1.173	0.661	
R_2R_8	-0.152	-0.124	-0.030	-0.191	
R_2R_9	0.097	0.088	-0.154	0.023	
R_2R_{10}	-0.164	-0.126	-0.126	-0.265	
R_2R_{11}	0.127	0.188	0.024	0.056	
R_3R_4	0.692	0.730	0.920	0.799	
R_3R_5	-0.327	-0.283	-0.781	-0.253	
R_3R_8	0.121	0.110	0.020	0.172	
R_3R_9	-0.113	-0.099	0.050	0.046	
R_3R_{10}	0.079	0.071	0.030	0.022	
R_4R_9	0.247	0.136	0.099	0.090	

(b) Remainder of Computed Force Field of Naphthalene

$r_1^2/2$	5.132	$\beta_1^2/2$	0.512	$r_1\beta_1$	-0.005	δ_1R_1	0.000	$\delta_1\beta_1$	-0.001	$\gamma_1\gamma_7$	0.000
$r_2^2/2$	5.166	$\beta_2^2/2$	0.510	$r_2\beta_1$	0.007	δ_1R_2	-0.121	$\delta_1\beta_2$	-0.003	$\gamma_1\gamma_8$	-0.003
r_1r_2	0.015	$\beta_1\beta_2$	0.007	$r_3\beta_1$	-0.007	δ_1R_3	-0.025	$\delta_1\beta_5$	-0.006	$\gamma_2\gamma_3$	-0.045
r_1r_3	0.004	$\beta_1\beta_3$	0.010	$r_4\beta_1$	0.000	δ_1R_4	0.000	$\delta_1\beta_6$	-0.010	$\gamma_2\gamma_6$	0.000
r_1r_4	0.002	$\beta_1\beta_4$	0.001	$r_5\beta_1$	0.009	δ_1R_7	-0.202	$\delta_2\beta_1$	-0.003	$\gamma_2\gamma_7$	0.000
r_1r_5	0.011	$\beta_1\beta_5$	0.003	$r_6\beta_1$	0.000	δ_1R_8	-0.064	$\delta_2\beta_2$	0.070	$\sigma_1\gamma_1$	-0.135
r_1r_6	0.001	$\beta_1\beta_6$	0.000	$r_7\beta_1$	0.000	δ_1R_9	0.000	$\delta_2\beta_5$	-0.009	$\sigma_1\gamma_2$	0.141
r_1r_7	0.000	$\beta_1\beta_7$	0.000	$r_8\beta_1$	0.003	δ_2R_1	-0.075	$\delta_2\beta_6$	0.006	$\sigma_1\gamma_5$	-0.011
r_1r_8	0.002	$\beta_1\beta_8$	0.003	$r_1\beta_2$	-0.007	δ_2R_2	0.203	$\delta_3\beta_1$	-0.072	$\sigma_1\gamma_6$	0.004
r_2r_3	0.014	$\beta_2\beta_3$	-0.009	$r_2\beta_2$	0.009	δ_2R_3	0.067	$\delta_3\beta_2$	0.040	$\sigma_2\gamma_1$	0.145
r_2r_6	0.001	$\beta_2\beta_6$	0.001	$r_3\beta_2$	0.004	δ_2R_4	-0.308	$\delta_3\beta_5$	0.006	$\sigma_2\gamma_2$	-0.101
r_2r_7	0.001	$\beta_2\beta_7$	0.000	$r_4\beta_2$	-0.007	δ_2R_7	0.142	$\delta_3\beta_6$	0.008	$\sigma_2\gamma_5$	-0.001
R_1r_1	-0.018	$R_1\beta_1$	-0.002	$r_5\beta_2$	0.000	δ_2R_8	-0.029	$\delta_1^2/2$	1.445	$\sigma_2\gamma_6$	-0.005
R_1r_2	-0.020	$R_1\beta_2$	-0.014	$r_6\beta_2$	0.000	δ_2R_9	-0.138	$\delta_2^2/2$	1.395	$\sigma_3\gamma_1$	-0.043
R_2r_1	0.066	$R_2\beta_1$	0.180	$r_7\beta_2$	0.000	δ_3R_1	0.000	$\delta_3^2/2$	1.415	$\sigma_3\gamma_2$	0.117
R_2r_2	-0.001	$R_2\beta_2$	0.015	$r_8\beta_2$	0.001	δ_3R_2	-0.057	$\delta_1\delta_2$	0.000	$\sigma_3\gamma_5$	0.013
R_2r_3	-0.021	$R_2\beta_3$	0.022	$\sigma_1^2/2$	0.299	δ_3R_3	0.212	$\delta_1\delta_3$	-0.174	$\sigma_3\gamma_6$	-0.001
R_2r_4	-0.028	$R_2\beta_4$	-0.014	$\sigma_2^2/2$	0.311	δ_3R_4	0.000	$\delta_1\delta_4$	0.305		
R_2r_5	0.007	$R_2\beta_5$	-0.022	$\sigma_3^2/2$	0.240	δ_3R_7	0.205	$\delta_1\delta_5$	0.000		
R_2r_6	0.004	$R_2\beta_6$	0.002	$\sigma_1\sigma_2$	0.000	δ_3R_8	0.055	$\delta_1\delta_6$	-0.311		
R_2r_7	-0.003	$R_2\beta_7$	-0.007	$\sigma_1\sigma_3$	0.076	δ_3R_9	0.000	$\delta_2\delta_3$	0.000		
R_2r_8	0.002	$R_2\beta_8$	-0.002	$\sigma_1\sigma_4$	0.032	δ_1r_1	0.111	$\delta_2\delta_4$	0.000		
R_3r_1	0.092	$R_3\beta_1$	-0.182	$\sigma_1\sigma_5$	0.000	δ_1r_2	-0.105	$\delta_2\delta_5$	0.258		
R_3r_2	0.087	$R_3\beta_2$	0.177	$\sigma_1\sigma_6$	-0.013	δ_1r_5	0.006	$\delta_2\delta_6$	0.000		
R_3r_3	-0.008	$R_3\beta_3$	-0.015	$\sigma_2\sigma_3$	0.000	δ_1r_6	-0.007	$\delta_3\delta_4$	-0.311		
R_3r_4	-0.015	$R_3\beta_4$	0.011	$\sigma_2\sigma_4$	0.000	δ_2r_1	-0.109	$\delta_3\delta_5$	0.000		
R_3r_5	0.002	$R_3\beta_5$	0.005	$\sigma_2\sigma_5$	0.011	δ_2r_2	0.052	$\delta_3\delta_6$	0.293		
R_3r_6	0.005	$R_3\beta_6$	0.009	$\sigma_2\sigma_6$	0.000	δ_2r_5	-0.011	$\gamma_1^2/2$	0.427		
R_3r_7	0.002	$R_3\beta_7$	0.004	$\sigma_3\sigma_5$	0.000	δ_2r_6	0.006	$\gamma_2^2/2$	0.436		
R_3r_8	0.007	$R_3\beta_8$	0.006	$\sigma_3\sigma_6$	-0.003	δ_3r_1	-0.005	$\gamma_1\gamma_2$	-0.094		
R_4r_1	-0.001	$R_4\beta_1$	0.001	$\Omega^2/2$	0.372	δ_3r_2	-0.084	$\gamma_1\gamma_3$	0.000		
R_4r_2	0.078	$R_4\beta_2$	-0.163	$\gamma_1\Omega$	-0.031	δ_3r_5	-0.008	$\gamma_1\gamma_4$	-0.017		
R_4r_5	0.007	$R_4\beta_5$	-0.001	$\gamma_2\Omega$	-0.017	δ_3r_6	0.005	$\gamma_1\gamma_5$	-0.004		
R_4r_6	-0.006	$R_4\beta_6$	-0.011	$\Omega\sigma_2$	-0.054			$\gamma_1\gamma_6$	-0.003		

[a] The units are consistent with energy in mdyn Å, R in Å, and angles in radians. [b] See text for reconstruction of this force field.

where the ab initio force constants are very small, such as the CH–CH stretching interactions, the CNDO/2 values (not reproduced here) are also very small. The greatest disagreement is in the CC-ring deformation space where the ab initio and CNDO/2 values often differ by a factor of about 2.

It can be seen from the force constants of Table II that, while some similarities exist, the naphthalene force field is quite different from that of benzene, particularly in the CC–CC interactions. Hence, it is expected that a naphthalene force field built up by a simple transfer of benzene force field elements would poorly reproduce the naphthalene fundamental vibrational frequencies.

Because of the uncertainties in the experimental force fields of naphthalene, we turn to a consideration of the vibrational spectrum provided by the computed force field as a test of the latter.

Vibrational Spectra of Naphthalene

The calculated spectra of the $C_{10}H_8$ and $C_{10}D_8$ forms of naphthalene shown in Tables III–V were obtained directly from the calculated force field of Table II. Experimental spectral data are given for comparison. Exact numerical agreement cannot be expected since the calculations assume harmonic oscillations while the molecule is of course anharmonic. Nevertheless, the overall excellent level of agreement leads us to believe that differences greater than about 10 cm⁻¹ between experimental and observed frequencies require some examination. In some cases there have

Table III. In-Plane Frequencies of Naphthalene[a]

	d_0		motion	d_8	
	calcd	exptl		calcd	exptl
A_g	505	514 g	δ_2	486	493 g
	757	761 g	R_1	689	692 g
	1023	1020 g	R_4	860	863 g
	1170	1144 sd, 1163 sd	$\beta_2 > \beta_1$	838	835 m
	1385	1380 g	$R_1 > R_3 > R_2$	1385	1386 g
	1458	1460 sn	$\beta_1 > \beta_2$	1287	1298 g
	1590	1578 sn	$R_3 > R_1 > R_2$	1563	1553 m
B_{3g}	512	508 g	δ_3	495	491 g
	940	939 g	δ_1	879	883 g
	1156	1099 g, 1145 sn, 1158 sn, 1168 sd	$R_3 \simeq \beta_2 > \beta_1$	1030	1027 g
	1255	1240 av	$\beta_1 > R_2 >> \beta_2$	833	828 g
	1458	1436 av, 1445 sd, 1458 sd	$\beta_2 >> R_2 > R_3$	1359	1330 m, 1353 g
	1644	1624 av	$R_3 \simeq R_2$	1617	1574 sn, 1605 sd
B_{1u}	354	359 g	δ_1	323	326 g
	792	748 g, 810 sd	$\delta_1 > R_2 > \delta_3$	737	734 sn
	1137	1125 g	$\beta_1 > \delta_1 > R_3 > \beta_1$	882	885 g, sn
	1272	1265 g	$\beta_1 > R_2 > \delta_1$	1049	1045 sd
	1391	1389 g	$\beta_2 > \beta_1 > R_2$	1248	1260 g
	1595	1595 g	R_3	1546	1545 g
B_{2u}	626	619 g	δ_2	600	594 g
	1003	1008 g	$R_4 >> R_3$	826	828 g
	1158	1144 sd, 1163 sn	$\beta_1 > \beta_2 >> R_3 \simeq R_2$	840	828 sd, 840 sn
	1204	1209 g	$R_2 >> \beta_2$	1081	1089 g
	1341	1361 g	$R_3 >> \beta_1$	1288	1290 g, 1312 g, 1318 g
	1515	1509 g	$R_4 > \beta_2 > R_2 > \beta_1$	1446	1384 sn, 1403 g, 1445 g

[a] Frequencies in cm^{-1}. For experimental values, sd, sn, m, and g indicate solid, solution, melt, and gas; av indicates a phase-averaged value.

Table IV. Out-of-Plane Frequencies of Naphthalene[a]

	d_0		motion	d_8	
	calcd	exptl		calcd	exptl
A_u	188		σ_3	169	
	622		$\sigma_1(\gamma_2,\gamma_1)$	531	
	825		γ_1	647	
	981		γ_2	815	
B_{3u}	172	166 g	Ω	159	153
	480	474 g	σ_2	404	404 sn, 408 sn, 401 g
	777	780 g	$\gamma_2(\gamma_1)$	627	629 g
	969	955 g	γ_1	797	791 g
B_{1g}	387	385 g	σ_2	341	350 g, 348 sd, 339 sn
	705	620 g, 717 sn	$\gamma_2,\gamma_1(\sigma_1)$	532	545 sd, 541 sn
	952	951 sd	γ_1,γ_2	761	766 sd, 784 m, 777 sn
B_{2g}	471	395 g, 465 sd, 470 sd	σ_3	413	413 m
	773	465 g, 772 sd	$\sigma_1(\gamma_2)$	634	646 sn, 671 sn
	879	875 av	$\gamma_1(\gamma_2)$	766	761 sd
	987	983 sd	$\gamma_2,\gamma_1(\sigma_1,\gamma_1)$	857	839 sd, 875 sn

[a] See Table III for meaning of symbols.

been questions raised previously about certain of the experimental assignments, or the present work suggests that the assignments may have been incorrect. Another difficulty may arise from Fermi resonance perturbing a given vibrational level. In either of these situations, it would be expected that good agreement would be obtained for one isotopic species but not the other.

Comments on the accuracy of the spectral assignments and the accuracy of the frequency predictions can most usefully be made according to the symmetry class of the various fundamentals. Because of their close spacing and large anharmonicity, the C–H frequencies (Table V) are not included in the discussion of the skeletal modes.

1. In-Plane Frequencies (Table III). A_g Modes. Some of the conflicting assignments considered by Neto et al.[36] seem to be resolved by the explanation that the assignments belong to the same mode in different phases (solid, solution, gas). Behlen et al.[30] considered for the first time the assignment of the symmetric CCH in-plane deformational mode to be 1163 cm^{-1} instead of the previously accepted value of 1144 cm^{-1} which Hanson and Gee[24] had favored earlier, suggesting that the 1163-cm^{-1} band be taken as a combination band. Our calculated value of 1170 cm^{-1} supports the assignment of Behlen et al., particularly in light of the fact that the corresponding prediction for the d_8 species gives excellent agreement.

Table V. CH Stretching Frequencies of Naphthalene[a]

	d_0		d_8	
	calcd	exptl	calcd	exptl
A_g	3056	3031 sn, 3004 sd, 3025 m	2257	2276 sd, 2257 m
	3085	3060 sn, 3055 sd	2289	2291 sd, 2272 m
B_{3g}	3047	3006 sd, 3060 sn, 2980 m, 3055 sd	2246	2261 sd, 2257 m, 2272 m
	3067	3092 sn, 3055 sd	2273	2276 sd. 2302 m
B_{1u}	3049	3058 g, 3055 sd, 3029 sn	2249	2266 m, 2232 sn, 2278 sn
	3070	3065 g, 3056 sn	2275	2284 m, 2278 sn, 2295 sn
B_{2u}	3052	3027 sn, 3005 sn. 3029 sn	2253	2248 m, 2258 sn
	3083	3090 g, 3056 sn	2288	2290 g, 2284 m, 2295 sn, 2278 sn

[a] See Table III for meaning of symbols.

B_{3g} Modes. The assignments of 1158[33] and 1168-cm^{-1}[24] for the B_{3g} d_0 mode ($R_3 + \beta$ mode) are the liquid and solid frequencies for the same vibration. However, assignments of 1099[34] and 1145 cm^{-1}[21] have also been proposed. Our calculations provide strong support for the choice made by Krainov.[33]

Hanson[24] chose the assignment of 1445 over 1458 cm^{-1} for the B_{3g} d_0 mode on the basis of intensity, but Stenman's reported Raman intensities[25] do not show a significant difference between these two modes. Our calculated frequency for the corresponding vibration in the deuterated compound is 29 cm^{-1} above the accepted assignment of 1330 cm^{-1}. This d_8 assignment is, however, considered doubtful by some authors,[23,30] since it has only been seen by Luther et al.[10] Therefore, a reasonable alternative to the 1445/1330-cm^{-1} pair for the d_0/d_8 assignment is the 1458/1353-cm^{-1} pair of bands.[12,24]

The $B_{3g}d_8$ asignment of 1574 cm^{-1} [36] persists in recent attempts to derive force fields for naphthalene from observed frequencies[37] despite the then ten-year-old convincing work of Bree and Kydd.[23] Krainov's 20-year-old interpretation of the naphthalene spectrum[33] agrees with Bree and Kydd on this point. Our calculated value is also in support of the higher frequency Bree assignment. There should no longer be any doubt as to this assignment.

Our calculated values of 1255 and 1644 cm^{-1} for the $B_{3g}d_0$ frequencies are 15 and 20 cm^{-1} too high, respectively. However, since no alternative assignments are evident, we conclude that this disagreement is an anharmonic effect that is lessened by deuteration.

B_{1u} Modes. The infrared-active B_{1u} fundamental vibration assigned variously to 748[33] or 810 cm^{-1} [35-37] has, in our opinion, probably never been identified. The 810-cm^{-1} band can be rejected since Rich and Dows[32] demonstrated that it disappears at low temperatures. The 748-cm^{-1} band is impossibly far from our predicted d_0 frequency of 792 cm^{-1}. Our calculated ab initio infrared intensity (see below) of 1.44 km/mol shows this band to be one of the weaker bands in the d_0 spectrum. If the true frequency were 3 cm^{-1} below the calculated value (as is observed for the corresponding vibration in the d_8 species), the band center would be around 789 cm^{-1}, separated from the very intense B_{3u} band at 780 cm^{-1} by only about 9 cm^{-1}. With an intensity ratio on the order of B_{1u}/B_{3u} = 0.011, we believe that only a high-resolution experiment will detect this fundamental. The other calculated B_{1u} modes agree very well with the accepted assignments.

B_{2u} Modes. The assignment of 1144 cm^{-1} as a B_{2u} fundamental has been widely accepted. The corresponding d_8 is, however, in doubt.[30] The infrared band observed by Mitra and Bernstein[21] and by Luther et al.[10] at 1163 cm^{-1} is only slightly less intense than the 1138-cm^{-1} (liquid)/1144-cm^{-1} (crystal) band.[21] Considering the lack of strong experimental evidence in favor of the 1144-cm^{-1} assignment and the acknowledged uncertainty in the d_8 assignment,[30] we propose 1163[10,21] and 840 cm^{-1} [10] as an alternative d_0 and d_8 assignment. Our results also confirm the recently reassigned $B_{2u}d_8$ fundamental at 1445 cm^{-1}.[30]

There is a major discrepancy (20 cm^{-1}) in our fit to the 1361-cm^{-1} d_0 assignment and uncertainty in the corresponding d_8 experimental assignment. This transition shows extreme sensitivity to the inter-ring CC–CC coupling constants which have no counterpart in the benzene spectrum from which scale factors were transferred. We believe that the experimental d_0 assignment is correct and that the discrepancy reflects a limitation in our procedure of scale factor transfer.

It is to be expected that a better fitting of the experimental spectrum of naphthalene could have been achieved by not treating it as a completely unknown molecule but rather by adjusting scale constants to give the best fit between its known spectrum and the directly computed force field. Such a procedure would not serve our purpose of testing the transferability of scale factors between related molecules and establishing the accuracy of a prior prediction of vibration spectra, but it should give the best information for the resolution of questionable assignments. We have, in fact, done this, including the 1361-cm^{-1} band along with other known frequencies but omitting any assignment for the corresponding d_8 band. The resulting force field gave frequency predictions of 1357 and 1310 cm^{-1} for this mode in the two isotopic species. Aside from giving much better agreement in the d_0 species, this result strengthens our belief in the previously doubted[30] assignment of 1312 cm^{-1} for the d_8 fundamental. Other changes in the

predicted spectra were trivial, but there were small improvements which reduced the overall average deviation from 6.5 to 4.2 cm^{-1}, excluding CH stretches. None of the other conclusions about questionable assignments were affected.

2. Out-of-Plane Modes (Table IV). Very little experimental basis exists for the assignment of the inactive A_u out-of-plane modes. Workers have attempted to assign the A_u vibrations from the set of observed crystal bands that have not been observed in the solution- or gas-phase spectra.[21] Considering the accuracy of previous calculations by this method for the benzene[6] and pyridine[1] spectra, as well as the other results presented here, we consider our calculated A_u frequencies (Table IV) to be the best available estimates (within about 10 cm^{-1}) of the true band centers.

The agreement between the calculated and observed B_{3u} frequencies is quite satisfactory, although the 14-cm^{-1} deviation between the calculated and observed B_{3u} $d_0\gamma_1$ frequencies is a bit more than is usual.

In the B_{1g} species Behlen et al.[30] prefer the assignment of 620 cm^{-1} as a $B_{1g}d_0$ CH wagging fundamental. It seems clear on the basis of our calculations that this assignment is incorrect and the true fundamental is at about 717 cm^{-1}.[10] The $B_{1g}d_8$ band at 766 cm^{-1} reported by Pietila and Stenman[26] agrees well with our calculated value of 761 cm^{-1}. Theirs is a solid-phase frequency, but the tendency is for the frequency to decrease slightly in going from the solid to the gas.

On the basis of our calculations we consider the recent reassignments[30] of 395 and 465 cm^{-1} for the lowest two $B_{2g}d_0$ fundamentals to be incorrect and that the older assignments of 470[26] (or 465[25]) and 772 cm^{-1} [24] are the true fundamentals. We also conclude that the $B_{2g}d_8$ solid-phase frequency of 646 cm^{-1} [25] is more probably the fundamental than is the 671-cm^{-1} band assigned by Lippincott and O'Reilly.[18] There is, however, a difficulty with the highest B_{2g} d_8 frequency. In spite of the 18-cm^{-1} discrepancy, we were unable to find a plausible alternative assignment in the literature. Considering the accuracy of our corresponding $B_{2g}d_0$ frequency, we feel that this d_8 band is likely obscured by the very intense A_g band at 862 cm^{-1}.[23]

3. C–H Stretching Frequencies (Table V). The computed C–H stretching frequencies are shown in Table V together with a number of alternative experimental assignments. These closely spaced fundamentals are undoubtedly perturbed by Fermi interactions which are not considered in the computed predictions. This, together with the nearly complete uncertainty in any experimental distinction between the bands, makes any detailed comparison unprofitable. It is interesting to note, however, that the frequency prediction of the total groups of bands is very good even though C–H vibrations are quite anharmonic. The behavior is evidence of the manner in which our procedure transfers similarities in anharmonicity between molecules as well as similarities in computational error.

4. Computed Infrared Absorption Intensities (Table VI). Dipole moment derivatives and the corresponding infrared absorption intensities have been computed and are shown in Table VI. The moderate-sized basis set used here is sufficient to produce, after scaling, an accurate force field and fundamental frequencies, but it is not adequate to give quantitatively accurate intensities. The results in Table VI must, therefore, be considered to have only qualitative significance. They are certainly sufficiently accurate to distinguish between the "strong", "medium", and "weak" designations that are commonly assigned experimentally.

Equilibrium Geometry of Naphthalene

The computed equilibrium geometry of naphthalene using the same computational techniques as in the present work has been reported previously.[44] We now propose to refine that geometry by fitting a set of predicted vibrational frequencies to the corresponding observed ones.

The idea of correlating fundamental vibrational frequencies with structural parameters is not new. McKean,[52] for example, has

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(52) D. C. McKean, J. E. Boggs, and L. Schäfer, *J. Mol. Struct.*, **116**, 313–330 (1984), and earlier works by McKean referred to therein.

Vibrational Spectrum of Naphthalene

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Table VI. Band Centers (cm^{-1}) and Infrared Intensities (km/mol)

	d_0		d_8	
	ν	intensity	ν	intensity
B_{3u}	172	2.51	159	2.39
	480	23.74	404	28.41
	777	126.68	627	48.16
	969	4.61	797	6.98
B_{2u}	626	4.65	600	4.75
	1003	2.62	826	3.27
	1158	1.38	840	1.08
	1204	1.17	1081	0.16
	1341	1.93	1288	0.47
	1515	10.22	1446	4.10
	3052	1.09	2253	1.40
	3083	53.95	2288	28.56
B_{1u}	354	2.25	323	1.89
	792	1.44	737	0.12
	1137	2.67	882	6.10
	1272	3.60	1049	0.13
	1391	5.72	1248	4.00
	1595	8.64	1546	2.15
	3049	1.66	2249	0.19
	3070	63.53	2275	41.75

Table VII. Structure of Naphthalene[a]

	X-ray			electron diffr		ab initio	
	CS[b]	PFA[c]	BD[d]	ABD[e]	KF[f]	SB[g]	SPB[h]
R_1	1.418	1.421	1.424	1.420	1.412	1.415	1.426
R_2	1.421	1.424	1.425	1.422	1.422	1.425	1.424
R_3	1.364	1.377	1.377	1.371	1.381	1.371	1.373
R_4	1.415	1.411	1.417	1.412	1.417	1.420	1.417
δ	0.055	0.043	0.046	0.048	0.038	0.051	0.049

[a] Distance in Å. See Figure 1 for definition of parameters.
[b] Cruickshank and Sparks, ref 41. [c] Ponomarev, Filipenko, and Atovmyan, ref 43. [d] Brock and Dunitz, ref 46. [e] Almenningen, Bastiansen, and Dyvik, ref 42. [f] Ketkar and Fink, ref 45. [g] Sellers and Boggs, ref 44. [h] This work.

shown that "isolated" CH stretching frequencies are a rather sensitive indicator of bond length. Owing to the impossibility of "isolating" CC vibrations, McKean's method cannot be directly extended to the determination of CC bond lengths. We attack the problem from the opposite direction, that is, by predicting frequencies from the geometry. In this fitting, the questionable assignments discussed above were given a zero weight, and gas-phase frequencies were preferred to solution or solid frequencies.

The cubic force constants are needed, at least approximately, to correct the harmonic force field of Table II for the effect of variation in the naphthalene geometry. The corrections were approximated as follows. The 4-21 diagonal cubic CH stretching force constant and the cubic CC-β^2 interaction constants were taken from the benzene calculation of Pulay et al.[6] The values of -0.828 mdyn/rad^2 for the important $R_3\gamma^2$ interaction was obtained from a linear interpolation between benzene and ethylene. The geometrically corrected quadratic force field (except for the diagonal CC's which were graphically determined) was then obtained by:

$$F_{ij}' = F_{ij} + \sum_k F_{ijk}\Delta q_k$$

where $\Delta q_k = q_k - q_{eq,k}$, q_k is some internal coordinate, and $q_{eq,k}$ is the value of q_k in the theoretical zero-force geometry.

Since the cluster of CC distances R_1–R_2–R_4 is experimentally more resolvable from the short-distance R_3 than the cluster members are from each other, we consider the following parameter in comparing structures:

$$\delta = \frac{1}{7}[R_1 + 4R_2 + 2R_4] - R_3$$

Table VII gives the bond lengths and δ values from several previous structure determinations.[42-45] The δ values are seen to range from 0.038 to 0.055 Å.

Table VIII gives a comparison of some frequencies obtained from various proposed structures of naphthalene-d_0. These frequencies are certain in their assignments and moderately to strongly dependent on the length of R_3. The in-plane modes are particularly sensitive to R_3 with the B_{1u} mode varying 50 cm^{-1} among the structures presented. Together with similar results for naphthalene-d_8, these data are suggestive of the corrctness of our value for R_3. Estimating that vibrational effects could lengthen R_3 by about 0.003–0.005 Å, the equilibrium R_3 of ref 43 and 46 should correspond to somewhere between 1.372 and 1.374 Å. The values of 1.381 Å reported in ref 45 and 1.364 Å reported in ref 41 and their respective δ values seem to lie outside the admissible range.

It is difficult to assess the accuracy of the spectroscopically refined geometry in a strongly coupled system like naphthalene. Nevertheless, we feel confident that the important bond length difference parameter δ = 0.049 Å is accurate to within a few thousandths of an Å.

Conclusions

The technique for deriving a scaled quantum mechanical (SQM) force field, which has recently been described in considerable detail,[8] has been shown to be remarkably successful in an evaluation of the complete harmonic force field and in the prediction of the vibrational harmonic frequencies of naphthalene. Transfer of scale constants derived by fitting to the observed spectrum of benzene[6] enabled high accuracy to be achieved in predicting a prior the vibrational spectrum of pyridine.[1] The same scale constants have now been used without modification to derive the naphthalene force field and predict its vibrational spectrum. With the exclusion of CH stretching frequencies, the average deviation between prediction and observation is 6.5 cm^{-1}. The largest deviation, 20 cm^{-1}, corresponded to a B_{2u} motion which shows a greater sensitivity to CC–CC coupling constants than it does to any of the diagonal force constants. Inter-ring CC–CC interactions have no direct counterpart in the benzene molecule, so it is understandable that they would be less accurately scaled by transfer of constants from benzene.

From the high accuracy of the predictions of vibrational fundamental frequencies it is clear that the scaling procedure is correcting not only for computational errors due to use of a finite basis set and neglect of electron correlation but also, to a degree that may perhaps be surprising, for effects of anharmonicity and perturbations that are similar between the molecule under study and the reference molecule.

The results presented here for naphthalene, the earlier results for pyridine, and those for smaller unsaturated molecules[8] all lead us to believe that ab initio computation at a relatively modest level

Table VIII. Frequencies Obtained from Proposed Structures of Naphthalene[a]

	X-ray			electron diffr		ab initio		
	CS	PFA	BD	ABD	KF	SB	SPB	exptl
A_g	1413	1388	1378	1396	1390	1395	1387	1380
A_g	1601	1582	1573	1589	1581	1584	1581	1578
B_{1g}	958	948	949	951	945	953	952	951
B_{2g}	994	982	983	982	978	985	987	983
B_{1u}	1615	1578	1574	1597	1564	1585	1589	1595
B_{3u}	976	965	963	972	962	971	969	955
Δ	18.50	6.17	7.17	8	11	8	5.83	

[a] References as given in footnotes to Table VII. Experimental values from Tables III and IV.

coupled with transfer of scale constants between related molecules can serve as a practical and highly reliable tool for the accurate prediction of infrared spectra.

Registry No. $C_{10}H_8$, 91-20-3; $C_{10}D_8$, 1146-65-2.

Phosphorus–Nitrogen Multiple Bonds. A Theoretical Investigation of Structure and Bonding in (NH)₂PNH₂, (NH₂)₂PN, and the (Cyclic) Dimer P₂N₆H₈

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Abstract: Results of extended basis set treatments on the SCF level and with inclusion of correlation effects are reported for various geometries of (NH)₂PNH₂, (NH₂)₂PN, and the dimer P₂N₆H₈. These molecules are considered as models for recently investigated compounds containing SiMe₃ or isopropyl instead of H. Computed geometric structure constants are in excellent agreement with experiment as far as a comparison is possible. On the highest level of theory, (NH)₂PNH₂ is found to be 22 kcal/mol lower in energy than the isomer (NH₂)₂PN, but dimerization to P₂N₆H₈ is exothermic by 45 kcal/mol. A detailed investigation of the electronic structures reveals that phosphorus is best considered as a tetravalent P⁺ in all compounds considered. The present results indicate (NH₂)₂PN to be a highly reactive molecule, quite different from (NH)₂PNH₂.

1. Introduction

Phosphorus(V) compounds usually show coordination numbers 4 to 6. The first planar, threefold coordinated phosphorus compound, PN₃R₄ (**1**, R = SiMe₃), was obtained[1,2] and investigated[3,4] a decade ago. The existence of the isomer **2** (for R = *i*-Pr, isopropyl) has recently been postulated as a short-lived intermediate[5] which undergoes, e.g., a head-to-tail cycloaddition[6] to
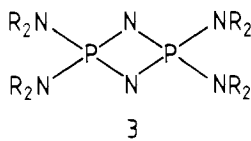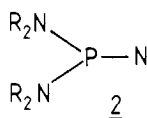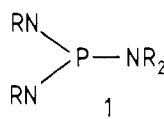
form the PN four-ring system P₂N₆R₈ (**3**). Molecule **1** is valence isoelectronic to PO₂Cl which according to recent experimental and theoretical investigations[7] is also planar.

The electronic structure in compounds **1–3** is so far not well understood (see, e.g., ref 4), and the basic question is: are stable double or triple PN bonds (e.g., RN=P in **1** and P≡N in **2**) formed in **1,2** or dominates the ionic character which would imply high reactivity. In order to answer this question we have performed extended ab initio calculations which will be reported in this paper. For this purpose we treated only the simplest possible case, R = H. This is a simplification, but since R serves mainly to saturate the valences of N, this should have no appreciable effect on the electronic structure of the PN₃ system in **1** or **2**, or the P₂N₆ system in **3**. The large groups R = SiMe₃ or R = *i*-Pr serve mainly to protect the PN bonds sterically and lead to some stabilization due to their appreciable polarizability.

A thorough investigation of possible PN double and triple bonds has been published by Trinquier[8] for the simplest possible cases: H₂NP, NPH₂, and HPNH. It was found that the electronic structure of singlet H₂PN is best described as H₂P=N, rather than H₂P≡N, and that H₂PN has only "somewhat triple-bond character". However, H₂PN and its isomers constitute rather simplified model cases for **1** and **2**, and a treatment of the more realistic molecules **1** to **3** (for R = H) appeared appropriate.

2. Details of Computation

The calculations were performed with the Karlsruhe version[9] of the "Columbus system of programs".[10] Geometry optimizations were carried out on the SCF level by means of a gradient program.[11] The following CGTO basis sets were employed:

P:	(11,7,1)/[6,4,1]	$\eta(d) = 0.4$
N:	(9,5,1)/[5,3,1]	$\eta(d) = 0.8$
H:	(4)/[2]	

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