the lithium salt of II, compared to the potassium salt, are consistent with the behavior of the stearic acid salts.

The near constancy of $\Delta G^{\ddagger}$ for rotation in all of our systems implies the existence of a compensation mechanism and, indeed, plotting $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ using the data in Tables II and III gives an excellent line with a slope corresponding to a compensation temperature of 325 K. This value is close to those observed for conformational changes in proteins.[30] Although the light scattering data indicate no temperature dependence of the micelle shape, the partial molar volumes for carboxylate salts are usually slightly temperature dependent.[31] We have observed an apparent change in transverse relaxation time with temperature, consistent with a "loosening" of molecular motion at higher temperatures, and its is possible that variations of the chemical shifts with temperature occur in a temperature range where we could not detect them. If improperly controlled, either of these factors could lead to systematic errors in our activation parameters, and it has already been noted that such errors can contribute to an apparent linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[32] Thus, the question of compensation behavior in our micellar system should be approached cautiously.

There appears to be little effect on the kinetics of rotation about the carbonyl carbon–nitrogen bond of sodium *N*-(dodecyloxycarbonyl)sarcosinate when this molecule is incorporated into a micelle. A rather loose structure for the micelle is indicated, and the major effect observed, in agreement with earlier work,[7] is a biasing of the conformational equilibrium to favor the most extended form of the detergent.

Acknowledgment. This work was supported by Grant GM-26469 from the National Institutes of Health. The Colorado State University Regional NMR Facility is supported by Grant CHE 78-18581 from the NSF while the Southern California Regional NMR Facility is supported by Grant CHE 79 16324A1. We are indebted to the staffs of the regional facilities for their assistance.

Registry No. I ($R^1 = \mathrm{C_{12}H_{23}}$, $R^2 = \mathrm{CH_2CO_2Na}$), 82639-79-0; I ($R^1 = \mathrm{C_{12}H_{23}}$, $R^2 = \mathrm{CH_2CO_2Li}$), 82639-80-3; I ($R^1 = \mathrm{C_{12}H_{23}}$, $R^2 = \mathrm{CH_2CO_2K}$), 82639-81-4; I ($R^1 = \mathrm{MeO_2C}$, $R^2 = \mathrm{CH_2CO_2Na}$), 82639-82-5; phosgene, 75-44-5; 1-dodecanol, 112-53-8; sarcosine, 53998-08-6; dodecyl chloroformate, 24460-74-0; methyl chloroformate, 79-22-1.

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Self-Consistent Molecular Orbital Methods. 24. Supplemented Small Split-Valence Basis Sets for Second-Row Elements

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Abstract: The recently introduced 3-21G split-valence basis sets for second-row elements have been supplemented with functions of d-type symmetry. The resulting basis sets, termed 3-21G$^{(*)}$, are for use in conjuction with unsupplemented 3-21G representations for first-row elements. Equilibrium structures calculated by using 3-21G$^{(*)}$ are generally in good accord with available experimental data and are markedly improved over the corresponding 3-21G level geometries, especially for hypervalent compounds and for molecules incorporating bonds between two second-row elements. 3-21G$^{(*)}$ level normal-mode vibration frequencies, hydrogenation energies, and electric dipole moments are also generally but not always in better agreement with their respective experimental quantities than are those obtained by using the unsupplemented 3-21G basis set. Overall, the 3-21G$^{(*)}$ basis set yields molecular properties that are uniformly close to those obtained with the much larger 6-31G* representation. The 3-21G$^{(*)}$ basis set is still relatively compact and as such is generally applicable to molecules of moderate size.

Introduction

The classical octet rule is frequently violated in compounds incorporating second-row elements. Lewis structures drawn for such "hypervalent" species as PF_5 and SF_6 depict valence manifolds comprising 10 and 12 electrons, respectively, more than the 8 electrons normally associated with a completely filled s and p shell. That such compounds exist and often exhibit high thermochemical stability is due to the availability for bonding of unfilled but low-lying d-type atomic orbitals on the second-row element. The concept of d-orbital participation in the bonding of hypervalent compounds has been repeatedly confirmed by quantitative molecular orbital calculations.[2]

The simplest levels of molecular orbital theory developed for compounds comprising second-row elements generally do not incorporate functions of d-type symmetry in the atomic basis set. It is not surprising, therefore, that such methods are apt to perform poorly in their description of the bonding in molecules containing a second-row element with an expanded valence shell. For example, while both the widely used minimal STO-3G[3] and split-

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(1) (a) University of California. (b) Carnegie-Mellon University. (c) Sandia Laboratory.

(2) E. E. Ball, M. A. Ratner, and J. R. Sabin, *Chem. Scr.*, **12**, 128–141 (1977), and references therein.

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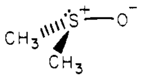
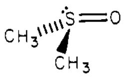
valence 3-21G[4] basis sets are moderately successful in reproducing the experimental equilibrium geometries of a variety of compounds incorporating normal-valent second-row elements, both methods fare very badly in their attempted descriptions of the structures of hypervalent species. The case of dimethyl sulfoxide is typical. Here, both STO-3G and 3-21G level calculations suggest a description in terms of a zwitterionic structure, **1a**, in which the sulfur atom is essentially normal valent. A more correct representation is, of course, **1b** where the valence orbital manifold about sulfur accommodates 10 electrons.


1a


1b

Numerous attempts have been made to construct simple and hence widely applicable atomic basis sets that allow for the description of hypervalent molecules.[5] Among the most simple is the STO-3G* representation,[6] formed from STO-3G by the addition of a set of five pure d-type Gaussians. The limited number of applications that have been carried out at this level suggest that the STO-3G* basis set is moderately successful in accounting for the geometrical structures of hypervalent molecules. For example, the experimental geometry of dimethyl sulfoxide is well reproduced. Failings of the simple theory are, however, apparent upon closer scrutiny. For example, the calculated equilibrium structures of hypervalent molecules such as PF_5 and ClF_3 fail to depict the observed significant differences between axial and equitorial bond distances. Furthermore, the STO-3G* basis set, like the minimal STO-3G representation on which it is constructed, is likely to perform very poorly both in the description of the relative energies of isomers and in the calculation of normal mode vibrational frequencies. Favorable performance in both of these areas, as well as in the description of equilibrium geometry, are the principal goals of any general structure theory.

The recently formulated 6-31G* polarization basis set for second-row elements[7] does perform satisfactorily in all three of these tasks. Equilibrium geometries calculated at this level both for normal-valent and hypervalent molecules are uniformly in close accord with experimental structures. Calculated normal-mode vibration frequencies are larger than the corresponding experimental values, although the errors in the theoretical quantities are relatively constant in magnitude. Experimental heats of hydrogenation for normal-valent molecules are reasonably well reproduced by the 6-31G* level calculations. The corresponding reaction heats for hypervalent species are not as well described, although they are markedly improved over the corresponding quantities calculated by using smaller basis sets.

The 6-31G* basis set for second-row elements is complete enough so as to provide a reasonable framework for approximate treatments of electron correlation. Previous experience with first-row molecules suggests that smaller minimal- and split-valence basis sets are not suitable for use in post-Hartree–Fock schemes.[8]

Unfortunately the 6-31G* basis set is too large, both in terms of number of atomic basis functions and number of primitive Gaussians, to be widely applicable to even moderately sized molecules. In practice, its application is limited to molecules comprising four to five heavy (nonhydrogen) atoms at most. Computations involving evaluation of energy derivatives (as is required for geometry optimization and frequency calculation) are strongly dependent on the number of Gaussian primitives in the basis set and are especially costly at the 6-31G* level. It is highly desirable, therefore, to have available a somewhat smaller and computationally more efficient basis set able to mimic the properties of the full 6-31G* polarization representation. In particular, such a basis set should be capable not only of accurately reproducing the known equilibrium geometries of molecules incorporating second-row elements with normal and expanded valence-shell electronic configurations but also should provide a satisfactory account of the relative energies and vibrational frequencies of both normal-valent and hypervalent species.

Table I. Calculated and Experimental Equilibrium Geometries for One-Heavy-Atom Hydrides (Bond Lengths (Å) and Angles (Deg))

molecule	point group	geom parameter	3-21G	3-21G$^{(*)}$	exptl
NaH[a]	$C_{\infty v}$	r(NaH)	1.926	1.923	1.887
MgH_2	$D_{\infty h}$	r(MgH)	1.726	1.723	
AlH_3	D_{3h}	r(AlH)	1.599	1.587	
SiH_4[b]	T_d	r(SiH)	1.487	1.475	1.481
PH_3[b]	C_{3v}	r(PH)	1.423	1.402	1.420
		∠(HPH)	96.1	95.2	93.3
H_2S[b]	C_{2v}	r(SH)	1.350	1.327	1.336
		∠(HSH)	95.8	94.4	92.1
HCl[a]	$C_{\infty v}$	r(ClH)	1.293	1.267	1.275

[a] Experimental data from D. R. Stull and J. Prophet, "JANAF Thermochemical Tables", 2nd ed., NSRDS-NBS 37, National Bureau of Standards, Washington, D.C., 1971. [b] Experimental data from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, "Structure Data on Free Polyatomic Molecules", Landolt-Bornstein, New Series, Group II, Vol. 7, K. H. Hellwege and A. M. Hellwege, Eds., Springer-Verlag, West Berlin, 1976.

Our starting point is the recently introduced 3-21G split-valence basis set, now defined for first-[4a] and second-row[4b] elements. It utilizes three Gaussian functions for all inner-shell atomic orbitals and has two sets of valence orbitals, written in terms of two and one Gaussian functions. The basis set is small enough to be widely applicable to molecules of moderate size. In fact, it comprises the same number of Gaussian primitives as the STO-3G minimal basis set, although these are distributed among twice the number of basis functions in the valence space. Therefore, 3-21G calculations that are heavily dominated by the integral evaluation steps required for derivative evaluation are only slightly higher in cost than those at minimal basis set STO-3G level, while "single-point" 3-21G calculations, which are often dominated by the SCF procedure (which depends directly only on the number of basis functions and not on their primitive makeup) will be significantly (~factor of 2) more costly.

To this simple split-valence representation we now propose to add a single set of second-order Gaussian functions, but only to second-row elements. By so limiting the supplementary functions we hope to realize a basis set that, while similar in construction to 6-31G*, will be smaller and hence more widely applicable.

Formulation of 3-21G$^{(*)}$ Basis Sets

3-21G$^{(*)}$ basis sets for second-row elements are constructed directly from the corresponding 3-21G representations by the addition of a complete set of six second-order Gaussian primitives. Although the resulting representations comprise the same number of atomic basis functions per second-row atom as the 6-31G* full-polarization basis set previously described,[7] these are made up of significantly fewer Gaussian primitives, (three instead of six for each inner-shell atomic orbital and two Gaussians instead of three for the innermost part of the valence description). In addition, descriptions for hydrogen, helium, and all first-row elements are in terms of unsupplemented 3-21G basis sets. Therefore, 3-21G$^{(*)}$, unlike 6-31G*, should not be viewed as a full-polarized basis set; rather it is best seen as a representation that, in as simple a manner as possible, is able to account for the participation of d-symmetry functions in the bonding about second-row atoms.

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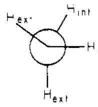
(8) See, for example (a) C. E. Dykstra and H. F. Schaefer in "The Chemistry of Ketenes and Allenes", S. Patai, Ed., Wiley, New York, 1980, p 1; (b) D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, *101*, 4085 (1979).

Table II. Calculated and Experimental Geometries for Two-Heavy-Atom Hydrides (Bond Lengths (Å) and Angles (Deg))

molecule	point group	geom parameter	3-21G	3-21G$^{(*)}$	exptl
LiCl[a]	$C_{\infty v}$	r(LiCl)	2.112	2.091	2.021
CH_3SiH_3[b]	C_{3v}	r(CSi)	1.917	1.883	1.867
		r(CH)	1.085	1.087	1.093
		r(SiH)	1.490	1.477	1.485
		$\angle$(HCH)	108.3	107.8	107.7
		$\angle$(HSiH)	108.3	108.3	108.3
HCP[c]	$C_{\infty v}$	r(CP)	1.548	1.513	1.542
		r(CH)	1.057	1.059	1.068
H_2CPH[d]	C_s	r(CP)	1.683	1.645	1.67
		$r(CH_{anti})$	1.073	1.076	
		$r(CH_{syn})$	1.073	1.074	
		r(PH)	1.433	1.408	
		$\angle(H_{anti}CP)$	119.5	119.9	
		$\angle(H_{syn}CP)$	124.7	125.1	
		$\angle$(HPC)	98.8	99.0	100
CH_3PH_2[c,e]	C_s	r(CP)	1.908	1.855	1.863
		$r(CH_{tr})$	1.081	1.082	1.093
		$r(CH_g)$	1.082	1.084	1.093
		r(PH)	1.425	1.404	1.414
		$\angle(PCH_{tr})$	112.1	113.0	109.2
		$\angle(PCH_gH_{g'})$	123.5	124.1	
		$\angle(H_gCH_{g'})$	108.9	107.7	109.7
		$\angle(CPHH')$	101.8	102.3	
		$\angle$(HPH)	95.6	94.6	93.4
CS[a]	$C_{\infty v}$	r(CS)	1.564	1.522	1.535
H_2CS[b]	C_{2v}	r(CS)	1.638	1.594	1.611
		r(CH)	1.073	1.076	1.093
		$\angle$(HCH)	116.5	115.3	116.9
CH_3SH[b,f]	C_s	r(CS)	1.895	1.823	1.819
		$r(CH_{tr})$	1.078	1.081	1.091
		$r(CH_g)$	1.077	1.080	1.091
		r(SH)	1.352	1.327	1.336
		$\angle(SCH_{tr})$	105.6	106.9	
		$\angle(SCH_gH_{g'})$	126.6	128.9	
		$\angle(H_gCH_{g'})$	111.4	110.1	109.8
		$\angle$(CSH)	97.9	97.5	96.5
CH_3Cl[c]	C_{3v}	r(CCl)	1.892	1.806	1.778
		r(CH)	1.073	1.076	1.086
		$\angle$(HCH)	112.6	110.8	110.7
PN[a]	$C_{\infty v}$	r(PN)	1.510	1.462	1.491
NaOH[a]	$C_{\infty v}$	r(NaO)	1.870	1.856	1.95
		r(OH)	0.962	0.963	0.96
MgO[a]	$C_{\infty v}$	r(MgO)	1.776	1.728	1.749
SiO[a]	$C_{\infty v}$	r(SiO)	1.536	1.496	1.509
HPO[b]	C_s	r(PO)	1.544	1.471	1.512
		r(PH)	1.447	1.429	
		$\angle$(HPO)	103.5	106.0	104.7
HOCl[c]	C_s	r(OCl)	1.767	1.700	1.690
		r(OH)	0.975	0.973	0.967
		$\angle$(HOCl)	104.2	106.1	102.5
NaF[a]	$C_{\infty v}$	r(NaF)	1.863	1.821	1.926
SiH_3F[b]	C_{3v}	r(SiF)	1.635	1.593	1.596
		r(SiH)	1.478	1.469	1.480
		$\angle$(HSiH)	109.8	109.9	110.6
ClF[a]	$C_{\infty v}$	r(ClF)	1.689	1.636	1.628
Na_2[a]	$D_{\infty h}$	r(NaNa)	3.228	2.465	3.078
NaCl[a]	$C_{\infty v}$	r(NaCl)	2.421	2.379	2.361
Si_2H_6[b]	D_{3d}	r(SiSi)	2.382	2.342	2.327
		r(SiH)	1.488	1.478	1.486
		$\angle$(HSiH)	108.8	108.6	107.9
SiH_3Cl[c]	C_{3v}	r(SiCl)	2.191	2.056	2.049
		r(SiH)	1.475	1.467	1.485
		r(HSiH)	111.8	110.5	108.7
P_2[a]	$D_{\infty h}$	r(PP)	1.930	1.853	1.894
P_2H_4[b,g]	C_2	r(PP)	2.356	2.205	2.219
		$r(PH_{int})$	1.421	1.401	1.417
		$r(PH_{ext})$	1.419	1.400	1.414
		$\angle(PPH_{int})$	99.1	100.6	99.1
		$\angle(PPH_{ext})$	95.5	96.3	94.3
		$\angle(H_{int}PPH_{ext})$	95.8	95.2	92.0
		$\omega(H_{int}PPH_{ext})$	79.1	73.0	74.0
HSSH[c]	C_2	r(SS)	2.264	2.057	2.058
		r(SH)	1.352	1.327	1.345
		$\angle$(SSH)	96.7	99.0	98.1
		ω(HSSH)	93.7	89.9	90.8
Cl_2[a]	$D_{\infty h}$	r(ClCl)	2.193	1.996	1.988

[a] See footnote *a* of Table I for reference to experimental data. [b] See footnote *b* of Table I for reference to experimental data. [c] Experimental data from M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data, 8*, 619 (1979). [d] The CP bond length and $\angle$(HPC) were determined by assuming CH bond lengths and HCH bond angles from $CH_2{=}NH$ and the PH bond length from $(CH_3)_2PH$. M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. E. Simmons, *J. Chem. Soc., Chem. Commun.*, 513 (1976). [e] Subscripts tr, g, and g' refer to relative orientations of the CH bonds to the phosphorus lone pair of 180° and ±60°, respectively. $PCH_gH_{g'}$ refers to the angle between the PC bond and the line bisecting the $H_gCH_{g'}$ plane. CPHH' refers to the angle between the CP bond and the line bisecting the HPH plane. [f] Subscripts tr, g, and g' refer to relative orientations of the SH and CH bonds of 180° and ±60°, respectively. $SCH_gH_{g'}$ refers to the angle between the SC bond and the line bisecting the $H_gCH_{g'}$ plane. [g] Subscripts int and ext refer to the projection



Average radial exponents, α, defining the set of d-type functions and suitable for use in calculations on molecules, are taken directly from previous work on the 6-31G* basis set.[7] These are 0.175, 0.175, 0.325, 0.45, 0.55, 0.65, 0.75, and 0.85 for the elements sodium to argon, respectively. Such values should closely approximate exponents that are appropriate for the addition of a single set of d-type functions to a completely saturated s- and p-type basis set.

Performance of the 3-21G$^{(*)}$ Basis Set

All molecular calculations have been performed with either the GAUSSIAN 83[9] or the GAUSSIAN 80[10] computer programs.

Equilibrium Geometries. Table I lists calculated (3-21G and 3-21G$^{(*)}$ basis sets) and, where available, experimental equilibrium geometries for the set of one-heavy-atom hydrides of second-row elements. The addition of d functions to the split-valence 3-21G basis set leads to a decrease in calculated bond lengths, the effect being most pronounced for the hydrides of the more electronegative elements. With the exception of sodium hydride, bond lengths calculated at the 3-21G$^{(*)}$ level are shorter than the corresponding experimental values; bond lengths obtained with the unsupplemented 3-21G basis set are uniformly longer than the experimental quantities. Mean absolute deviations from experiment in calculated bond lengths for the 3-21G and 3-21G$^{(*)}$ basis sets are 0.016 and 0.015 Å, respectively. Thus, the addition of second-order functions to the 3-21G basis set does not lead to improvement in the calculated XH bond lengths in the one-heavy-atom, second-row hydrides.

Calculated 3-21G$^{(*)}$ equilibrium bond angles in PH_3 and in H_2S are in reasonable accord with the corresponding experimental

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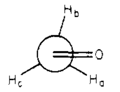
(9) D. J. DeFrees, B. A. Levi, S. K. Pollack, E. S. Blurock, R. F. Hout, Jr., W. J. Pietro, M. M. Francl, and W. J. Hehre, to be submitted for publication.

(10) J. S. Binkley, R. A. Whiteside, R. Krishnan, H. B. Schlegel, R. Seeger, D. J. DeFrees, and J. A. Pople, submitted to the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

Table III. Calculated and Experimental Equilibrium Geometries for Hypervalent Molecules (Bond Lengths (Å) and Angles (Deg))

molecule	point group	geom parameter	3-21G	3-21G$^{(*)}$	exptl^{a}
PF_5	D_{3h}	$r(\mathrm{PF_{eq}})$	1.580	1.538	1.534
		$r(\mathrm{PF_{ax}})$	1.604	1.566	1.577
$(CH_3)_3PO^{b}$	C_{3v}	$r(\mathrm{PO})$	1.598	1.478	1.479
		$r(\mathrm{PC})$	1.849	1.805	1.813
		$r(\mathrm{CH_{tr}})$	1.083	1.086	1.099
		$r(\mathrm{CH_{g}})$	1.082	1.085	1.099
		$\angle(\mathrm{CPC})$	103.6	103.9	106.0
		$\angle(\mathrm{H_{tr}CP})$	110.7	112.1	
		$\angle(\mathrm{PCH_gH_{g'}})$	125.1	125.4	
		$\angle(\mathrm{H_gCH_{g'}})$	108.4	107.6	
F_3PO	C_{3v}	$r(\mathrm{PO})$	1.506	1.427	1.436
		$r(\mathrm{PF})$	1.575	1.527	1.524
		$\angle(\mathrm{FPF})$	100.0	100.8	101.3
F_3PS	C_{3v}	$r(\mathrm{PS})$	2.042	1.855	1.866
		$r(\mathrm{PF})$	1.589	1.537	1.538
		$\angle(\mathrm{FPF})$	98.5	99.3	99.6
SO_2	C_{2v}	$r(\mathrm{SO})$	1.526	1.419	1.431
		$\angle(\mathrm{OSO})$	114.0	118.7	119.3
$(CH_3)_2SO^{c}$	C_s	$r(\mathrm{SO})$	1.678	1.490	1.477
		$r(\mathrm{SC})$	1.862	1.791	1.810
		$r(\mathrm{CH_a})$	1.079	1.082	1.054
		$r(\mathrm{CH_b})$	1.078	1.083	1.097
		$r(\mathrm{CH_c})$	1.078	1.082	1.093
		$\angle(\mathrm{CSO})$	105.0	107.8	106.7
		$\angle(\mathrm{CSC})$	98.1	96.6	96.4
		$\angle(\mathrm{SCH_a})$	108.0	108.0	108.3
		$\angle(\mathrm{SCH_b})$	109.2	110.2	108.2
		$\angle(\mathrm{SCH_c})$	106.7	110.3	109.6
		$\angle(\mathrm{H_aCH_b})$	112.0	108.6	113.6
		$\angle(\mathrm{H_aCH_c})$	109.8	109.2	106.6
		$\omega(\mathrm{H_aCSO})$	48.0	66.4	
SF_4	C_{2v}	$r(\mathrm{SF_{eq}})$	1.616	1.550	1.545
		$r(\mathrm{SF_{ax}})$	1.677	1.617	1.646
		$\angle(\mathrm{F_{eq}SF_{eq}})$	107.4	101.7	101.6
		$\angle(\mathrm{F_{ax}SF_{ax}})$	162.8	169.8	173.1
F_2SO	C_s	$r(\mathrm{SO})$	1.529	1.414	1.413
		$r(\mathrm{SF})$	1.633	1.569	1.585
		$\angle(\mathrm{FSO})$	105.8	106.8	106.8
		$\angle(\mathrm{FSF})$	91.8	92.0	92.2
NSF	C_s	$r(\mathrm{SN})$	1.568	1.440	1.448
		$r(\mathrm{SF})$	1.671	1.609	1.643
		$\angle(\mathrm{NSF})$	107.8	113.8	116.9
SO_3	D_{3h}	$r(\mathrm{SO})$	1.532	1.411	1.420
$(CH_3)_2SO_2$	C_{2v}	$r(\mathrm{SO})$	1.592	1.438	1.431
		$r(\mathrm{SC})$	1.830	1.756	1.777
		$r(\mathrm{CH_{tr}})$	1.079	1.083	
		$r(\mathrm{CH_g})$	1.078	1.080	
		$\angle(\mathrm{OSO})$	119.1	119.5	121.0
		$\angle(\mathrm{CSC})$	102.7	102.8	103.3
		$\angle(\mathrm{H_{tr}CS})$	106.8	107.6	
		$\angle(\mathrm{SCH_gH_{g'}})$	124.4	127.9	
		$\angle(\mathrm{H_gCH_{g'}})$	112.2	110.4	
SF_6	O_h	$r(\mathrm{SF})$	1.612	1.550	1.564
F_4SO	C_{2v}	$r(\mathrm{SO})$	1.549	1.413	1.403
		$r(\mathrm{SF_{eq}})$	1.640	1.533	1.552
		$r(\mathrm{SF_{ax}})$	1.597	1.578	1.575
		$\angle(\mathrm{F_{eq}SF_{eq}})$	110.7	109.6	110.2
		$\angle(\mathrm{F_{ax}SF_{ax}})$	169.2	171.6	178.6
ClF_3	C_{2v}	$r(\mathrm{ClF_{ax}})$	1.757	1.676	1.698
		$r(\mathrm{ClF_{eq}})$	1.673	1.601	1.598
		$\angle(\mathrm{F_{ax}ClF_{ax}})$	167.2	171.0	175.0
ClF_5	C_{4v}	$r(\mathrm{ClF_{ax}})$	1.696	1.599	1.65
		$r(\mathrm{ClF_{eq}})$	1.715	1.624	1.65
		$\angle(\mathrm{F_{ax}ClF_{eq}})$	83.4	84.4	86.5
$FClO_2$	C_s	$r(\mathrm{ClO})$	2.244	1.430	1.418
		$r(\mathrm{ClF})$	1.678	1.618	1.697
		$\angle(\mathrm{OClO})$	109.8	114.9	115.2
		$\angle(\mathrm{OClF})$	104.9	102.1	101.7
$FClO_3$	C_{3v}	$r(\mathrm{ClO})$	2.302	1.408	1.404
		$r(\mathrm{ClF})$	1.676	1.574	1.619
		$\angle(\mathrm{OClO})$	113.6	115.3	116.6

[a] See footnote b of Table I for reference to experimental data. [b] Subscripts tr, g, and g' refer to relative orientations of the CH and PO bonds of 180° and ±60°, respectively. $\mathrm{PCH_gH_{g'}}$ refers to the angle between the PC bond and the line bisecting the $\mathrm{H_gCH_{g'}}$ plane. [c] Subscripts a, b, and c refer to the projection



[d] Subscripts tr, g, and g' refer to relative orientations of the CH bond and the sulfur lone pair of 180° and ±60°, respectively. $\mathrm{SCH_gH_{g'}}$ refers to the angle between the SC bond and the line bisecting the $\mathrm{H_gCH_{g'}}$ plane.

values and are marginally better than those obtained from 3-21G level calculations.

Calculated equilibrium geometries for the larger set of two-heavy-atom molecules containing one or two second-row elements are compared to experimental structures in Table II. As noted previously for one-heavy-atom molecules, the addition of the second-order functions generally leads to a reduction in bond length. The effect is greatest for linkages involving two heavy atoms and increases in importance roughly with increasing electronegativity of the component elements. In the majority of cases, equilibrium bond lengths calculated at the 3-21G$^{(*)}$ level are in better agreement with their respective experimental values than are those obtained with the unsupplemented 3-21G basis set. In some cases the improvement is dramatic, as for example in Cl_2 where the effect of the added d functions is to decrease the calculated bond distance by 0.197 Å, from 2.193 Å at the 3-21G level to 1.996 Å. The latter value is in good agreement with the experimental bond length of 1.988 Å. Similar decreases in calculated bond lengths, leading to equally impressive improvements in performance, are found for the PP linkage in diphosphine and for the SS bond in hydrogen disulfide. Lesser but often substantial changes are also noted for other single linkages involving two heavy atoms.

Calculated (3-21G$^{(*)}$ level) multiple bond lengths are consistently shorter than their respective experimental values, typically by 0.02–0.03 Å. This is the same general trend as has already been noted for the 3-21G basis set applied to molecules comprising first-row elements only. It is also consistent with the results of previously reported 6-31G* calculations.[7] On the other hand, the lengths of multiple bonds involving second-row elements are generally overestimated at the 3-21G level, the errors typically being on the order of 0.01–0.02 Å. These observations taken as a whole suggest that the supplemented 3-21G$^{(*)}$ basis sets for second-row elements are more appropriate companions for first-row 3-21G representations even for compounds described in terms of a normal complement of valence electrons.

The equilibrium bond length calculated for the very weakly bound Na_2 molecule at the 3-21G$^{(*)}$ level is more than 0.6 Å shorter than the experimental value. The separation obtained with the 3-21G basis set is in better agreement with the experimental data even though it is still in error (too long) by 0.15 Å.

With the exclusion of diatomic sodium, the mean absolute deviation from experiment of 3-21G$^{(*)}$ level calculated bond lengths between heavy atoms is 0.027 Å. This represents a marked improvement from the corresponding deviation of 0.071 Å resulting from 3-21G level calculations on the same set of molecules.

Calculated 3-21G$^{(*)}$ level bond angles are of roughly comparable quality to those obtained by using the unsupplemented 3-21G basis set and generally in reasonable accord with the available experimental data.

Equilibrium geometries for a number of simple molecules containing a second-row element with an expanded valence shell,

Table IV. Calculated and Experimental Normal-Mode Vibration Frequencies (cm^{-1})

molecule	symmetry of mode	description	3-21G// 3-21G	3-21G$^{(*)}$// 3-21G$^{(*)}$	exptl	
					measd[a]	harmonic
NaH[b]	σ		1170	1156	1172	1192
SiH_4[c,d]	a_1	sym str	2311	2398	2187	2377
	e	deg deform	1046	1057	975	975
	t_2	deg str	2285	2396	2191	2319
		deg deform	974	1021	914	945
PH_3[c,e]	a_1	sym str	2404	2608	2323	2452
		sym deform	1093	1145	992	1041
	e	deg str	2398	2598	2328	2457
		deg deform	1271	1288	1118	1154
H_2S[c,f]	a_1	sym str	2642	2903	2615	2722
		bend	1323	1381	1183	1215
	b_1	asym str	2656	2900	2626	2733
HCl[b]	σ		2847	3149	2990	3042
PF_5	a_1'	PF_3 sym str	867	917	816	
		PF_2 sym str	786	784	648	
	a_2''	PF_2 asym str	1164	1170	947	
		PF_3 deform	545	607	575	
	e'	PF_3 deg str	1180	1193	1024	
		PF_3 deg deform	508	563	533	
	e''	PF bend	191	187	174	
		PF bend	476	540	520	
SO_2[c,g]	a_1	sym str	1114	1341	1151	1167
	b_1	bend	497	602	518	526
		asym str	1297	1573	1362	1381
SO_3[h]	a_1'	sym str	926	1192	1065	1048
	a_2''	sym deform	356	543	498	504
	e'	deg str	1152	1537	1391	1409
	e''	deg deform	440	588	530	539
ClF_3	a_1	ClF str	826	930	752	
		ClF_2 sym str	581	636	529	
		ClF_2 deform	341	398	328	
	b_1	ClF_2 asym str	764	895	702	
		ClF_2 deform	421	485	442	
	b_2	ClF_2 deform	305	364	328	

[a] Measured vibrational frequencies from T. Shimanouchi, *J. Chem. Phys. Ref. Data, 6,* 993 (1977) (unless otherwise noted).

[b] Experimental data from G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, Van Nostrand Reinhold Co., New York, 1950.

[c] Measured vibrational frequencies from T. Shimanouchi, "Table of Molecular Vibrational Frequencies", consolidated Vol. I, NSRDS-NBS 39, National Bureau of Standards, Washington, D.C., 1972.

[d] Harmonic frequencies from I. W. Levin and W. T. King, *J. Chem. Phys., 37,* 1375 (1962).

[e] Harmonic frequencies from J. L. Duncan and I. M. Mills, *Spectrochim. Acta., 20,* 523 (1964).

[f] Harmonic frequencies from H. C. Allen, Jr., and E. K. Plyler, *J. Chem. Phys., 25,* 1132 (1956).

[g] Harmonic frequencies from R. D. Shelton, A. H. Nielsen, and W. H. Fletcher, *J. Chem. Phys., 21,* 2178 (1953).

[h] Harmonic frequencies from A. J. Dorney, A. R. Hoy, I. M. Mills, *J. Mol. Specrosc., 45,* 253 (1973).

calculated at both the 3-21G and 3-21G$^{(*)}$ levels, are compared to experimental structures in Table III. As previously noted, the unsupplemented split-valence basis set is generally unable to adequately account for the known geometries of such species. In particular, bonds to the second-row elements are consistently longer than the corresponding experimental quantities. The situation is at an extreme for multiple bonds, where errors in calculated lengths approaching 1 Å are noted (e.g., ClO linkages in $FClO_2$ and $FClO_3$). The poor performance is, of course, a direct consequence of the unavailability of basis functions of proper symmetry to construct the appropriate molecular orbitals.

The 3-21G$^{(*)}$ basis set appears to be quite successful in accounting for the structures of hypervalent molecules. The mean absolute deviation from experiment of calculated bond lengths involving two heavy atoms is only 0.015 Å, comparable to that noted for the previously discussed set of "normal-valent" compounds. For comparison, the corresponding mean absolute deviation for bond lengths calculated at the 3-21G level is 0.132 Å. The calculations also reproduce a number of subtle features in the geometrical structures of the references compounds. For example, the theory accurately reproduces the differences in axial and equitorial PF bond lengths in phosphorus pentafluoride and in quasi-axial and quasi-equitorial SF bond distances in sulfur tetrafluoride and in thionyl tetrafluoride. The theory is also successful in accounting for the measured bond-length differences in ClF_3. Its predictions regarding the significant differences in "axial" and "equitorial" bond distances in the pseudooctahedral ClF_5 molecule remain untested due to lack of refinement of the experimental structural data. The 3-21G$^{(*)}$ level calculations accurately mimic the observed shortening in the PO bond length as the methyl groups in trimethylphosphine oxide are replaced by fluorine atoms. This presumably is due to the effect of the highly electronegative fluorine atoms in lowering the energies of the (formally) vacant d orbitals on phosphorus, making them more available for bonding. Comparison of the experimental SO bond lengths in dimethyl sulfoxide and in thionyl fluoride shows a similar shortening. Again the calculations concur.

Only a limited number of examples of hypervalent molecules have been examined by us at the present time. It is impressive, however, given the diversity of the compounds, that the calculations appear not to have seriously erred, either in the assignment of structure to any given molecule or in any major trend in structure on going from one compound to another.

Normal-Mode Vibration Frequencies. A comparison of calculated (3-21G and 3-21G$^{(*)}$ levels) and measured normal-mode vibration frequencies for a selection of second-row, one-heavy-atom hydrides as well as for a few simple molecules incorporating elements with expanded valence shells is provided in Table IV. Where available, harmonic experimental frequencies (i.e., those corrected for anharmonicity) have been provided. With the exception of NaH, frequencies calculated at the 3-21G level for both sets of compounds are smaller than those obtained with the 3-21G$^{(*)}$ basis set. This presumably reflects the role of the added d-type functions in contributing to the bonding in molecules. 3-21G level frequencies are usually smaller than experimental harmonic values (except for NaH and HCl, they are larger than directly measured frequencies for normal-valent compounds). Errors are largest for hypervalent compounds, the calculated

Table V. Calculated 3-21G$^{(*)}$ Total Energies (Hartrees)

molecule	E(3-21G$^{(*)}$// 3-21G$^{(*)}$)	molecule	E(3-21G$^{(*)}$// 3-21G$^{(*)}$)
Na	−160.85505	NaF	−259.79462
Mg	−198.48529	MgO	−272.82782
Al	−240.58694	SiO	−361.94212
Si	−287.39447	SiH_3F	−388.19334
P	−339.05950	ClF	−556.21735
S	−395.63122	Na_2	−321.71057
Cl	−457.37109	NaCl	−618.34005
Ar	−524.44759	Si_2H_6	−578.42753
NaH	−161.38351	SiH_3Cl	−746.66985
MgH_2	−199.60341	P_2	−678.16971
AlH_3	−242.34374	P_2H_4	−680.48914
SiH_4	−289.78426	H_2S_2	−792.48318
PH_3	−340.81399	Cl_2	−914.75844
H_2S	−396.81964	PF_5	−833.83836
HCl	−457.98141	$(CH_3)_3PO$	−531.80016
LiCl	−464.88271	F_3PO	−710.44456
CH_3SiH_3	−328.62274	F_3PS	−1031.64117
HCP	−377.27220	SO_2	−544.50373
H_2CPH	−378.44631	$(CH_3)_2SO$	−548.84666
CH_3PH_2	−379.64109	SF_4	−791.20887
CS	−433.24608	F_2SO	−667.88295
H_2CS	−434.44646	NSF	−548.62764
CH_3SH	−435.63728	SO_3	−618.91500
CH_3Cl	−496.79500	$(CH_3)_2SO_2$	−623.30361
PN	−393.19949	SF_6	−989.04707
HPO	−414.08806	F_4SO	−865.63792
HOCl	−532.35417	ClF_3	−753.82308
NaOH	−235.88636	ClF_5	−951.43974
		$FClO_2$	−704.85800
		$FClO_3$	−779.21914

frequencies for which are often 20–30% smaller than measured values. This is consistent with the notion that lacking atomic functions of d symmetry, the 3-21G basis set is unable to account for the strong binding found in these compounds.

Except for NaH, all frequencies calculated at the 3-21G$^{(*)}$ level, both for normal-valent and hypervalent compounds are larger than spectroscopic values. It is to be noted, however, that the theoretical calculations at this level fare better overall for the normal-valent hydrides (maximum error of 17%) than they do for hypervalent species (maximum errors of 27%). The errors in frequencies noted here, both for 3-21G and 3-21G$^{(*)}$ level calculations, are not nearly as constant as those previously observed in applications of the theory to molecules comprising first-row elements only.[4a,11] This is especially true of the hypervalent compounds considered. It appears furthermore, that the problem does not reside (entirely) with the choice of basis set. Errors in vibrational frequencies calculated at the HF/6-31G* level for molecules containing second-row elements are not as uniform as those for analogous first-row systems. Whether this problem is due entirely to neglect of electron correlation effects or in part to limitations inherent to the use of quadratic force fields for highly coordinated (hypervalent) compounds remains a matter for future study. What is clear, however, is that because of the considerable variation in the magnitudes of errors in calculated frequencies, it is likely that neither the 3-21G nor the 3-21G$^{(*)}$ second-row basis sets will prove to be as useful as their first-row analogues as an aid to the assignment of vibrational spectra.

Relative Energies. A complete listing of 3-21G$^{(*)}$ total energies for the atoms and molecules dealt with in this paper is presented in Table V. For atoms, energy lowerings over the unsupplemented 3-21G basis set[4a] are for the most part due to the fact that the added set of six second-order Gaussians contributes a function of s symmetry to the basis set. This in turn serves to supplement the rather meager three Gaussian representations for the inner-shell 1s and 2s atomic orbitals. Energy lowerings corresponding to the addition of second-order Gaussians to the 6-31G basis set are an order of magnitude smaller.[7]

Experimental heats of formation both at 298 K and at 0 K for the molecules incorporating second-row elements dealt with in this paper are given in Table VI. Also included are the corre-

Table VI. Experimental Heats of Formation and Zero-Point Energies (kcal mol^{-1})

molecule[a]	$\Delta H_f°$(298 K)	$\Delta H_f°$(0 K)	E(zero point)
H_2[b]	0.0	0.0	6.3
LiH[b]	33.6	33.6	1.9
BeH_2	30.0	30.4	9.3
BH_3	25.0	26.4	18.0
CH_4[c]	−17.9	−16.0	27.1
NH_3[c]	−11.0	−9.3	20.6
H_2O[c]	−57.8	−57.1	12.9
HF[e]	−64.8	−64.8	5.9
NaH[b]	30 ± 5	30 ± 5	1.7
MgH_2			
AlH_3[d]			21.5
SiH[c]	7.3	10.1	19.2
PH_3[c,e]	1.3	2.8	14.6
H_2S[c]	−4.9	−4.2	9.2
HCl[b]	−22.1	−22.0	4.3
LiCl	−47 ± 3	−47 ± 3	0.9
CH_3SiH_3[e,f]	−4.0	−0.1	37.9
HCP	40 ± 15	40 ± 15	8.3
H_2CPH[d]			20.0
CH_3PH_2[d]			32.2
CS[b]	64.8	63.8	1.8
H_2CS[d,e]	24.3	25.2	14.8
CH_3SH[e,g]	−5.4	−2.9	31.2
CH_3Cl[e]	−20.7	−18.8	22.9
PN[b]	24	24	1.9
HPO[d]			6.6
HOCl[f]	−22 ± 3	−21 ± 3	8.0
NaOH	−50 ± 5	−49 ± 5	7.8
NaF	−69.4	−69.0	0.8
SiO	−24 ± 2	−24 ± 2	1.8
SiH_3F	−105 ± 15	−103 ± 15	16.9
ClF	−12.1	−12.1	1.1
Na_2	32.9	33.5	0.2
NaCl	−43.4	−43.0	0.5
Si_2H_6	17.0	21.0	30.4
SiH_3Cl	−48 ± 15	−46 ± 15	16.2
P_2	42.7	42.3	1.1
P_2H_4	5.0	7.6	20.3
H_2S_2	3.8	5.2	11.2
Cl_2	0.0	0.0	0.8
PF_5	−376.9	−374.7	10.7
$(CH_3)_3PO$	−102.2		
F_3PO	−296 ± 2	−294 ± 2	9.1
F_3PS	−237 ± 15	−236 ± 15	7.6
SO_2	−70.9	−70.2	4.3
$(CH_3)_2SO$	−36.0		
SF_4	−183 ± 5	−182 ± 5	7.1
F_2SO	−130 ± 5	−129 ± 5	5.8
NSF			3.4
SO_3	−94.6	−93.2	7.7
$(CH_3)_2SO_2$	−88.7		
SF_6	−291.7	−288.4	13.4
F_4SO	−226 ± 4		
ClF_3	−38.0	−37.0	4.4
ClF_5	−57 ± 15	−55 ± 15	8.4
$FClO_2$			
$FClO_3$	−5.1	−3.0	9.9

[a] Thermochemical data and vibrational frequencies from reference in footnote *a* of Table I, unless otherwise noted. [b] See footnote *e* of Table IV for reference to vibrational frequencies. [c] See footnote *b* of Table IV for reference to vibrational frequencies. [d] Frequencies calculated at the 3-21G level. [e] Thermochemical data from S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976. [f] See footnote *a* of Table IV for reference to vibrational frequencies. [g] Vibrational frequencies from L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, "Vibrational Spectra of Polyatomic Molecules", Wiley, New York, 1974.

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Table VII. Calculated and Experimental Energies of Complete Hydrogenation (kcal mol^{-1})

hydrogenation reaction	3-21G	3-21G$^{(*)}$	exptl[a]
$LiCl + H_2 \rightarrow LiH + HCl$	72	59	60 ± 3 (59)
$CH_3SiH_3 + H_2 \rightarrow CH_4 + SiH_4$	−11	−10	−8 (−7)
$HCP + 3H_2 \rightarrow CH_4 + PH_3$	−89	−94	−68 ± 15 (−57)
$H_2CPH + 2H_2 \rightarrow CH_4 + PH_3$	−59	−62	
$CH_3PH_2 + H_2 \rightarrow CH_4 + PH_3$	−16	−17	
$CS + 3H_2 \rightarrow CH_4 + H_2S$	−119	−114	−100 (−88)
$H_2CS + 2H_2 \rightarrow CH_4 + H_2S$	−62	−65	−54 (−47)
$CH_3SH + H_2 \rightarrow CH_4 + H_2S$	−20	−23	−16 (−17)
$CH_3Cl + H_2 \rightarrow CH_4 + HCl$	−21	−25	−21 (−19)
$PN + 3H_2 \rightarrow PH_3 + NH_3$	−78	−74	−45 (−34)
$HPO + 2H_2 \rightarrow PH_3 + H_2O$	−58	−11	
$HOCl + H_2 \rightarrow H_2O + HCl$	−54	−57	−61 ± 3 (−58)
$NaOH + H_2 \rightarrow NaH + H_2O$	16	25	21 ± 7 (22)
$NaF + H_2 \rightarrow NaH + HF$	30	46	34 ± 5 (35)
$MgO + 2H_2 \rightarrow MgH_2 + H_2O$	−87	−73	
$SiO + 3H_2 \rightarrow SiH_4 + H_2O$	−37	−37	−34 ± 3 (−27)
$SiH_3F + H_2 \rightarrow SiH_4 + HF$	31	45	46 ± 15 (48)
$ClF + H_2 \rightarrow HCl + HF$	−63	−64	−78 (−75)
$Na_2 + H_2 \rightarrow 2NaH$	44	42	30 ± 10 (27)
$NaCl + H_2 \rightarrow NaH + HCl$	73	62	52 ± 5 (51)
$SiH_3SiH_3 + H_2 \rightarrow 2SiH_4$	−8	−11	−3 (−2)
$SiH_3Cl + H_2 \rightarrow SiH_4 + HCl$	15	17	33 ± 15 (33)
$P_2 + 3H_2 \rightarrow 2PH_3$	−40	−56	−46 (−40)
$P_2H_4 + H_2 \rightarrow 2PH_3$	−8	−10	−5 (−2)
$HSSH + H_2 \rightarrow 2H_2S$	−19	−21	−14 (−14)
$Cl_2 + H_2 \rightarrow 2HCl$	−45	−51	−45 (−44)

[a] Experimental data are based on 0 K heats of formation and corrected for zero-point vibrational energy. Data based on 298 K heats and not corrected for zero-point energy follow in parentheses.

sponding data for H_2 and the first-row one-heavy-atom hydrides. These are required for the energy comparisons that follow. In some cases it was necessary to estimate the 0 K data from heats of formation obtained at 298 K by using the ideal gas relationships

$$\Delta H_{trans}(T) = H_{trans}(T) - H_{trans}(0) = \tfrac{3}{2}RT$$

$$\Delta H_{rot}(T) = H_{rot}(T) - H_{rot}(0) = RT \text{ (linear molecule)}$$
$$\tfrac{3}{2}RT \text{ (nonlinear molecule)}$$

$$\Delta H_{vib}(T) = H_{vib}(T) - H_{vib}(0) = N\sum_i h\nu_i/[\exp(h\nu_i/kT) - 1] + RT$$

where T is the temperature (298 K), R is the gas constant, N is Avagodro's number, h is Planck's constant, and the ν_i are the experimentally determined molecular vibration frequencies. Summation is over vibrational modes. Also included in Table VI are experimental zero-point vibration energies obtained from the expression

$$E_{zero\ point} = \tfrac{1}{2}\sum_i h\nu_i$$

Table VII compares calculated (3-21G and 3-21G$^{(*)}$ levels) and experimental energies of complete hydrogenation of the set of normal-valent, two-heavy-atom molecules discussed earlier. With few exceptions the added d functions have little effect on the reaction energies calculated with the 3-21G basis set. The largest changes generally occur for compounds incorporating either sodium or chlorine. Overall, the mean absolute deviations of calculated hydrogenation energies from experiment are nearly the same for the 3-21G and 3-21G$^{(*)}$ levels, 10 and 11 kcal mol^{-1}, respectively.

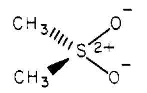
As expected, the corresponding theoretical hydrogenation energies for hypervalent compounds (Table VIII) are greatly affected by the addition of d functions to the 3-21G basis. For all cases involving hypervalent sulfur and chlorine, for which the hydrogenation processes as written are highly exothermic, the results of the 3-21G$^{(*)}$ calculations are in markedly better agreement with the experimental data than are those derived from the 3-21G basis set alone. Still, the mean absolute deviation of calculated (3-21G$^{(*)}$ level) hydrogenation energies from experiment for this set of compounds is 21 kcal mol^{-1}. For each of the hypervalent phosphorus compounds dealt with here, complete hydrogenation is significantly endothermic. While the 3-21G level calculations consistently underestimate the degree of endothermicity, calculations utilizing the 3-21G$^{(*)}$ basis set do the opposite. Overall, the two methods fare equally poorly in dealing with these compounds, mean absolute deviations of 3-21G and 3-21G$^{(*)}$ calculated hydrogenation energies being 72 and 30 kcal mol^{-1}, respectively.

Table VIII. Calculated and Experimental Energies of Complete Hydrogenation of Hypervalent Compounds (kcal mol^{-1})

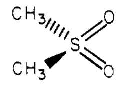
hydrogenation reaction	3-21G	3-21G$^{(*)}$	exptl[a]
$PF_5 + 4H_2 \rightarrow PH_3 + 5HF$	47	135	45 (54)
$(CH_3)_3PO + 4H_2 \rightarrow PH_3 + 3CH_4 + H_2O$	−66	−24	(−8)
$F_3PO + 4H_2 \rightarrow PH_3 + H_2O + 3HF$	5	98	34 ± 2 (45)
$F_3PS + 4H_2 \rightarrow PH_3 + H_2S + 3HF$	2	74	32 ± 15 (39)
$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$	−149	−75	−60 (−50)
$(CH_3)_2SO + 3H_2 \rightarrow H_2S + 2CH_4 + H_2O$	−123	−90	(−58)
$SF_4 + 3H_2 \rightarrow H_2S + 4HF$	−126	−52	−89 ± 5 (−81)
$F_2SO + 3H_2 \rightarrow H_2S + H_2O + 2HF$	−120	−47	−71 ± 5 (−62)
$NSF + 3H_2 \rightarrow H_2S + NH_3 + HF$	−136	−98	
$SO_3 + 4H_2 \rightarrow H_2S + 3H_2O$	−233	−107	−97 (−84)
$(CH_3)_2SO_2 + 4H_2 \rightarrow H_2S + 2CH_4 + 2H_2O$	−192	−94	(−68)
$SF_6 + 4H_2 \rightarrow H_2S + 6HF$	−177	−26	−111 (−102)
$F_4SO + 4H_2 \rightarrow H_2S + H_2O + 4HF$	−210	−73	(−96)
$ClF_3 + 2H_2 \rightarrow HCl + 3HF$	−288	−184	−184 (−179)
$ClF_5 + 3H_2 \rightarrow HCl + 5HF$	−405	−297	−298 ± 15 (−289)
$FClO_2 + 3H_2 \rightarrow HCl + 2H_2O + HF$	−304	−243	
$FClO_3 + 4H_2 \rightarrow HCl + 3H_2O + HF$	−426	−307	−269 (−255)

[a] See footnote *a* of Table VII.

Electric Dipole Moments. As the data in Table IX indicate, the addition of a single shell of d-type functions on second-row elements alone has a marked effect on calculated electric dipole moments. In general, dipole moments calculated at the 3-21G$^{(*)}$ level are in better accord with the experimental data than are those obtained with the unsupplemented 3-21G representation, mean absolute deviations from experiment being 0.44 and 0.90 D, respectively. The improvement is more conspicuous for hypervalent molecules than it is for normal-valent species. As noted previously, the 3-21G level calculations tend to overestimate the polarities of bonds involving elements with expanded valence-electron manifolds (e.g., preference for cannonical structures such as **2a**



2a



2b

in preference to **2b**). This in turn leads to an overestimation of local bond dipoles and, hence, generally to a poor description of the overall moment. The fact that dipole moments for such species as dimethyl sulfoxide and dimethyl sulfone calculated at the 3-21G$^{(*)}$ level are larger than their respective experimental values (but not nearly by as much as those obtained from the 3-21G basis set) suggests that, even at this level, local bond dipoles are overestimated.

Comparison of 3-21G$^{(*)}$ and 6-31G* Basis Sets

One of the principal objectives of the present research has been to produce a basis set, the performance of which not only is satisfactory in its own right but also mimics as closely as possible the behavior of the more flexible 6-31G* representation. It is, therefore, of interest to critically compare the performance of the 3-21G$^{(*)}$ and 6-31G* basis sets. It should at the outset be recognized that such a comparison is "rigged". The valence descriptions of both the 3-21G$^{(*)}$ and the 6-31G* basis sets ultimately derive from a common origin, and the supplementary shell of d-type functions are identical in the two representations. The most

Table IX. Calculated and Experimental Electric Dipole Moments (Debyes)

molecule	3-21G//3-21G	3-21G$^{(*)}$//3-21G$^{(*)}$	exptl[a]
NaH	7.01	6.93	6.96
PH_3	1.24	0.88	0.58
H_2S	1.83	1.42	0.97
HCl	1.86	1.54	1.08
LiCl	8.13	7.77	7.13
CH_3SiH_3	0.63	0.71	0.74
HCP	0.87	0.54	0.39
H_2CPH	1.48	1.14	
CH_3PH_2	1.39	1.21	1.10
CS	0.85	1.44	1.98
H_2CS	2.42	2.05	1.65[b]
CH_3SH	2.12	1.74	1.52
CH_3Cl	2.86	2.31	1.87
PN	2.36	2.67	2.75[c]
HPO	2.59	2.49	
HOCl	2.15	2.03	1.3[d]
NaOH	5.47	5.39	
NaF	7.54	7.25	8.16
MgO	5.65	6.85	
SiO	2.97	2.89	3.10[e]
SiH_3F	1.87	1.37	1.27
ClF	1.13	1.23	0.88
NaCl	10.16	9.47	9.00
SiH_3Cl	3.53	2.00	1.31
P_2H_4	1.76	1.39	0.93[f]
H_2S_2	1.93	1.57	
$(CH_3)_3PO$	5.08	4.41	
F_3PO	1.48	1.75	1.76
F_3PS	1.03	1.23	0.64
SO_2	2.98	2.29	1.63
$(CH_3)_2SO$	4.90	4.30	3.96
SF_4	2.21	1.37	0.63
F_2SO	3.17	2.40	1.63
NSF	2.14	2.16	1.90[g]
$(CH_3)_2SO_2$	6.15	4.98	4.49
F_4SO	1.54	1.75	
ClF_3	1.38	1.15	0.6
ClF_5	1.98	1.33	0.54[h]
$FClO_2$	0.96	2.55	1.72[i]
$FClO_3$	0.33	0.47	0.02

[a] Unless otherwise noted, experimental dipole moments are from R. D. Nelson, D. R. Lide, and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", NSRDS-NBS 10, National Bureau of Standards, Washington, D.C., 1967. [b] D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectrosc.*, *39*, 136 (1971). [c] J. Raymonda and W. J. Klemperer, *J. Chem. Phys.*, *55*, 232 (1971). [d] D. G. Lister and D. J. Millen, *Trans. Faraday Soc.*, *67*, 601, (1971). [e] J. W. Raymonda, J. S. Muenter, and W. Klemperer, *J. Chem. Phys.*, *52*, 3558 (1969). [f] J. R. Durig, L. A. Carreira, and J. D. Odom, *J. Am. Chem. Soc.*, *96*, 2688 (1974). [g] R. L. Cook and W. H. Kirchhoff, *J. Chem. Phys.*, *47*, 4521 (1967). [h] H. K. Bodench, W. Hüttner, and P. Nowicki, *Z. Naturforsch., A*, *31A*, 1638 (1976). [i] C. I. Parent and M. C. L. Gerry, *J. Mol. Spectrosc.* *49*, 343 (1974).

significant difference in the two basis sets is no doubt their treatment of first-row atoms. Whereas unsupplemented 3-21G representations for first-row elements are used in conjunction with 3-21G$^{(*)}$ second-row basis sets, the 6-31G* model allows for a d-type (polarization) function on all (first- and second-row) atoms. The effects of such added flexibility will probably exhibit themselves most clearly in the descriptions of molecules in which first-row (rather than second-row) elements comprise the primary structure. Other differences between the 3-21G$^{(*)}$ and 6-31G* basis sets (3 Gaussian as opposed to 6 Gaussian inner-shell representations and a 2:1 as opposed to a 3:1 valence-shell splitting) are probably of lesser consequence to overall performance.

Table X compares equilibrium geometries, normal-mode vibration frequencies, hydrogenation energies, and electric dipole moments for a number of normal-valent and hypervalent sulfur compounds calculated at the 3-21G$^{(*)}$ and 6-31G* levels. Experimental data, where available, are also tabulated.

Equilibrium structures calculated at the 3-21G$^{(*)}$ level are nearly identical with those obtained from the 6-31G* basis set. All bond distances agree to within 0.007 Å. Similarly, bond angles calculated with the 3-21G$^{(*)}$ basis set are consistently close (within 0.5°) to those obtained at the 6-31G* level.

Theoretical 3-21G$^{(*)}$ and 6-31G* normal-mode vibration frequencies are generally in close accord with each other, although individual deviations on the order of 20–30 cm^{-1} are common. Typically, but not always, the 3-21G$^{(*)}$ frequencies are smaller than the corresponding 6-31G* values (and hence closer to experiment). This is perhaps not entirely expected in view of the availability in the 6-31G* representation of d functions on first-row elements for participation in molecular binding.

Although calculated hydrogenation energies for the normal-valent sulfur compounds remain essentially unchanged in going from the 3-21G$^{(*)}$ to the 6-31G* basis sets, those for the two hypervalent compounds considered show greater sensitivity. While, as the data imply, the addition of polarization functions to first-row atoms benefits the normal-valent reaction products more than it does the hypervalent reactants, it is likely that part of the differences in hydrogenation energies is due to superposition effects associated with the smaller basis set. Thus, the valence functions on one center act to "patch up" deficiencies in the inner shells of the other centers. Hartree–Fock calculations with basis sets larger than 6-31G* have been carried out for CS.[12] The near-limiting Hartree–Fock hydrogenation energy for this molecule is −111 kcal mol^{-1}. Here, at least, superposition errors associated with 6-31G* appear to be small.

Calculated electric dipole moments show some sensitivity to the basis set both for normal-valent and hypervalent molecules. Significant variations are noted for H_2CS (0.19 D) and for CS and SO_2 (both 0.10 D).

Comparison of 3-21G$^{(*)}$ and MIDI-*i** Basis Sets

Minimal and split-valence basis sets termed MINI-*i** and MIDI-*i** for second-row molecules that provide polarization functions have recently been constructed.[13] Use of the latter representations in the calculation of molecular properties leads to a significantly improved description relative to either the unpolarized-parent basis, MIDI-*i*, or the corresponding minimal basis set, MINI-*i*, especially for hypervalent molecules. The MIDI-*i* basis is prepared in a manner that differs from that used in the present work. Three MIDI-*i** representations were constructed, with *i* = 1, 3, and 4; the smallest of which, MIDI-1*, is of the same size as our 3-21G$^{(*)}$ representation. The constraint imposed on the development of the 3-21G$^{(*)}$ basis, in which the same radial exponents are used for s and p functions of the same principle quantum number, is released for MIDI-1* leading to an increase in the amount of work necessary in the integral evaluation. The composition of the MIDI-1* basis differs in two respects from that of the 3-21G$^{(*)}$ representation. MIDI-1* does not include a polarization function of d symmetry on either Na or Mg, relying instead only on functions of p symmetry to provide sufficient polarization. However, while the 3-21G$^{(*)}$ basis for second-row atoms is used in conjunction with the unpolarized 3-21G representation for first-row atoms, the MIDI-1* basis is defined with polarization on all atoms, both first and second row. The radial exponents for MIDI-1* p and polarization functions are optimized on the atom for maximum overlap between the additional function and the valence orbital, in contrast to those used for 3-21G$^{(*)}$, which are taken from the larger, more flexible 6-31G* basis set.

Calculated molecular geometries from MIDI-1* are of nearly the same quality as those obtained from 3-21G$^{(*)}$ calculations. For the set of 12 molecules for which data for comparison were available, the optimum geometries from both MIDI-1* and 3-21G$^{(*)}$ are given in Table XI. Without Na_2, the mean deviation

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(12) Hartree–Fock limiting energies for CS from W. G. Richards, *Trans. Faraday Soc.*, *63*, 257 (1967); for H_2 and CH_4 from J. A. Pople and J. S. Binkley, *Mol. Phys.*, *29*, 599 (1975); for H_2S from M. Ahlström, B. Jöhsson, and G. Karlstrom, *ibid.*, *38*, 1051 (1979).

(13) (a) Y. Sakai, H. Tatewaki, and S. Huzinaga, *J. Compnt. Chem.* *2*, 100 (1981); (b) Y. Sakai, H. Tatewaki, and S. Huzinaga, *ibid.*, *2*, 108 (1981).

Table X. Comparison of 3-21G$^{(*)}$ and 6-31G* Equilibrium Structures, Normal-Mode Vibration Frequencies, Hydrogenation Energies, and Electric Dipole Moments

	equilibrium structure[a]				vibration frequencies,[b] cm^{-1}			hydrogenation energy, kcal mol^{-1}			dipole moment,[c] D		
molecule	parameter	3-21G$^{(*)}$	6-31G*	exptl	mode	3-21G$^{(*)}$	6-31G*	exptl	3-21G$^{(*)}$	6-31G*	exptl	3-21G$^{(*)}$	6-31G*	exptl
H_2S	r(SH)	1.327	1.326	1.336	a_1	2903	2918	2615				1.42	1.41	0.97
	∠(HSH)	94.4	94.4	92.1	a_1	1381	1368	1183						
					b_1	2900	2930	2626						
CS[d]	r(CS)	1.523	1.520	1.535	σ	1412	1471	1285	−114	−112	−100	1.44	1.34	1.98
H_2CS	r(CS)	1.594	1.597	1.611	a_1	3272	3303		−65	−64	−54	2.05	2.24	1.65
	r(CH)	1.076	1.078	1.093	a_1	1665	1658							
	∠(HCH)	115.3	115.5	116.9	a_1	1189	1180							
					b_1	3355	3393							
					b_1	1111	1097							
					b_2	1169	1158							
CH_3SH[e]	r(CS)	1.823	1.817	1.819	a′	3301	3322	3000	−23	−22	−19	1.74	1.79	1.52
	$r(CH_{tr})$	1.081	1.082	1.091	a′	3224	3236	2931						
	$r(CH_g)$	1.080	1.081	1.091	a′	2890	2908	2572						
	r(SH)	1.327	1.327	1.336	a′	1662	1655	1475						
	$\angle(SCH_{tr})$	106.9	106.7		a′	1541	1521	1319						
	$\angle(SCH_gH_{g'})$	128.9	129.3		a′	1233	1220	976						
	$\angle(H_gCH_{g'})$	110.1	110.0	109.8	a′	891	873	803						
	∠(CSH)	97.5	97.9	96.5	a′	745	776	708						
					a″	3301	3325	3000						
					a″	1638	1623	1430						
					a″	1093	1080	1074						
					a″	240	265							
H_2S_2[f]	r(SS)	2.057	2.063	2.055	a	2884	2904	2556	−21	−21	−14	1.57	1.58	
	r(SH)	1.327	1.327	1.327	a	1022	1014	883						
	∠(HSS)	99.0	99.2	91.3	a	549	568	509						
	∠(HSSH)	89.9	89.9	90.6	a	467	462	416						
					b	2883	2905	2559						
					b	1029	1019	886						
SO_2	r(SO)	1.419	1.414	1.431	a_1	1341	1357	1151	−75	−87	−60	2.29	2.19	1.63
	∠(OSO)	118.7	118.8	119.3	a_1	602	592	518						
					b_1	1573	1568	1362						
SO_3[f]	r(SO)	1.411	1.405	1.402	a_1'	1192	1227	1065	−107	−132	−97			
					a_2''	543	561	498						
					e′	1537	1555	1391						
					e″	588	584	530						

[a] See footnote *b* of Table I for reference to experimental data unless otherwise noted. [b] See footnote *b* of Table IV for reference to experimental data unless otherwise noted. [c] See footnote *a* of Table IX for reference to experimental data. [d] See footnote *a* of Table I for reference to experimental data. [e] See footnote *g* of Table VI for reference to experimental vibrational frequencies. [f] See footnote *a* of Table IV for reference to experimental vibrational frequencies.

from experiment for the 3-21G$^{(*)}$ and the MIDI-1* bond lengths were 0.016 and 0.010 Å, respectively. In both representations the weak Na–Na linkage is poorly described; 3-21G$^{(*)}$ finds it to be much shorter than the experimental values, while the MIDI-1* distance is significantly longer. Calculated bond angles from both basis sets are nearly identical. One would expect that the MIDI-1* basis would perform somewhat better than the 3-21G$^{(*)}$ representation in the calculation of molecular properties for compounds containing both first- and second-row atoms, since it provides polarization functions for both types of atoms. It is, however, consequently more costly to apply.

Conclusion

A simple basis set for second-row elements has been formulated. Termed 3-21G$^{(*)}$, it derives from the recently introduced 3-21G split-valence representation and allows for the proper description of the bonding in hypervalent molecules by way of the inclusion of supplementary functions of d-type symmetry. The following general conclusions regarding its performance may be drawn from the calculations reported in this paper.

(1) Equilibrium structures both for normal-valent and hypervalent molecules are uniformly in good accord with available experimental data. They are markedly improved over the corresponding 3-21G level structures, especially for compounds comprising second-row elements with expanded valence-electron manifolds and for molecules incorporating bonds between two second-row atoms.

(2) Normal-mode vibration frequencies obtained with the 3-21G$^{(*)}$ basis set are consistently larger than experimental values, generally by 10–20%. This is in contrast to the performance of the 3-21G level calculations, which yield frequencies both smaller and larger than the measured quantities. The relative consistency of errors in calculated frequencies suggests that, with proper scaling, the theory at this level might prove of some utility in the assignment of vibrational spectra.

Table XI. Comparison of 3-21G$^{(*)}$ and MIDI-1* Equilibrium Structures

molecule	parameter	3-21G$^{(*)}$	MIDI-1*[a]	exptl
NaH	r(NaH)	1.923	1.892	1.887
MgH_2	r(MgH)	1.723	1.699	1.709
SiH_4	r(SiH)	1.475	1.490	1.481
H_2S	r(SH)	1.327	1.343	1.336
	∠(HSH)	94.4	93.8	92.1
HCl	r(HCl)	1.267	1.278	1.275
NaCl	r(NaCl)	2.379	2.352	2.361
Na_2	r(NaNa)	2.465	3.235	3.078
P_2	r(PP)	1.853	1.871	1.894
Cl_2	r(ClCl)	1.996	2.202	1.988
ClF	r(ClF)	1.636	1.627	1.628
SO_2	r(SO)	1.419	1.437	1.431
	∠(OSO)	118.7	118.1	119.3
ClF_3	$r(ClF_{ax})$	1.676	1.678	1.698
	$r(ClF_{eq})$	1.601	1.591	1.598
	$\angle(F_{ax}ClF_{ax})$	171.0	170.8	175.0

[a] Optimized structures from work in ref 13b.

(3) Calculated 3-21G$^{(*)}$ level hydrogenation energies for normal-valent compounds are generally but not always closer to

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experimental values than are energies obtained from 3-21G level calculations. For the majority of hypervalent compounds the improvement is considerable, although deviations between calculated, 3-21G$^{(*)}$ level, and experimental hydrogenation energies are often large. Previous work has suggested the importance of electron correlation effects on calculated hydrogenation energies.

(4) Theoretical 3-21G$^{(*)}$ level electric dipole moments both for normal-valent and hypervalent compounds are consistently in better agreement with experimental values than are those obtained from the unsupplemented 3-21G basis set. Still, large discrepancies with experimental moments exist for some molecules.

(5) The 3-21G$^{(*)}$ basis set yields equilibrium structures and vibrational frequencies in close accord with those obtained from the 6-31G* basis set. Calculated hydrogenation energies and electric dipole moments differ is some systems by as much as 25%, although in these cases it is not always the larger 6-31G* basis set that is in better agreement with experiment.

The 3-21G$^{(*)}$ basis set is significantly less costly to apply than 6-31G*, the difference arising because of both a difference in number of Gaussian primitives employed and the lack of d-functions on first-row atoms. The exact cost differential varies widely, depending on the molecule (i.e., number of first-row elements) and on the particular task at hand (i.e., geometry optimization or frequency calculation, which are dominated by integral evaluation steps vs. single-point runs, which are often dominated by the SCF procedure); our own experience indicates a differential of between 4 and 6 times. Related to cost is range of application. Although 3-21G$^{(*)}$ and 6-31G* basis sets for hydrogen and for second-row atoms comprise the same number of atomic functions, they differ significantly in size for first-row elements (9 functions for 3-21G$^{(*)}$ vs. 15 for 6-31G*). Therefore, size (memory space) restrictions, while perhaps not influencing the selection of basis set for molecules comprising only hydrogen and second-row elements, are apt to be a more significant factor for molecules incorporating first-row atoms.

Acknowledgment. This research was supported in part by grants from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Na, 7440-23-5; Mg, 7439-95-4; Al, 7429-90-5; Si, 7440-21-3; P, 7723-14-0; S, 7704-34-9; Cl, 22537-15-1; Ar, 7440-37-1.

Micellar Dediazoniation: Dramatic Directive Effects on the Course of Reaction

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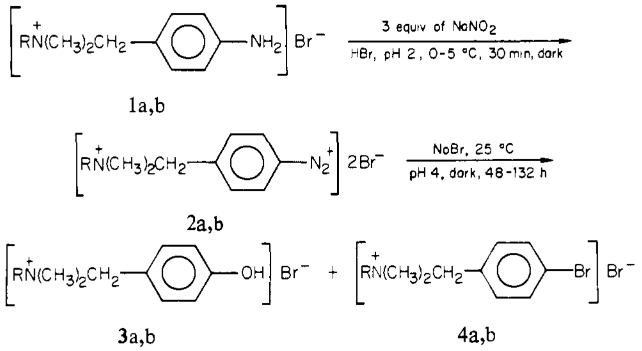
Abstract: Rate constants and products are reported for the dediazoniation reactions of nonmicellar (*p*-diazoniobenzyl)trimethylammonium dibromide and micellar (*p*-diazoniobenzyl)dimethyl-*n*-hexadecylammonium dibromide in aqueous solutions at pH 4, 23 °C, in the presence of various concentrations of bromide ion. Rate constants for the nonmicellar ($k \sim 6 \times 10^{-6}$ s^{-1}) and micellar ($k \sim 10^{-5}$ s^{-1}) dediazoniations were independent of bromide ions at concentrations ranging from 0.015 to 0.50 M, consistent with rate determining aryl cation formation in each case. However, product identity was strictly controlled by the reaction environment: in the concentration range $0.005 \leq [Br^-] \leq 0.050$ M, micellar dediazoniation gave only (>95%) the corresponding aryl bromide whereas nonmicellar dediazoniation gave only (>95%) the corresponding phenol.

Swain and co-workers established that the dediazoniations of simple aryldiazonium ions proceeded via rate-determining formation of aryl cations, which selected between available nucleophiles in rapid subsequent reactions.[1,2] The availability of cationic surfactant aromatic diazonium ions[3] suggested that we examine *micellar* dediazoniation. Two questions could be addressed: (1) Forced to proceed in the positively charged Stern layer of a cationic micelle, and in the presence of approximated, nucleophilic bromide counterions, would the rate limiting step of the dediazoniation process remain the formation of an aryl cation? (2) Could the unusual microenvironment provided by the cationic micelles significantly alter the selectivity of product formation? The results provide affirmative answers to both questions and, in the second case, the outcome is striking.

Scheme I[a]



[a] Series a, R = n-$C_{16}H_{33}$; series b, R = CH_3.

Results and Discussion

The necessary starting materials, anilinosurfactants **1a** and **1b**, were prepared and diazotized (to **2a** and **2b**) by published procedures.[3] The reactions of interest are summarized in Scheme I.

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(1) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783, et seq.

(2) Reviews: Bernasconi, C. F. *Chimia* **1980**, *34*, 1. Ambroz, H. B.; Kemp, T. J. *Chem. Soc. Rev.* **1979**, *8*, 353. Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141. Hegarty, A. F. In "The Chemistry of Diazonium and Diazo Groups", Part 2, Patai, S., Ed.; Wiley: New York, 1978; pp 511 f.

(3) Moss, R. A.; Rav-Acha, Ch. *J. Am. Chem. Soc.* **1980**, *102*, 5045.

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