nitrogen of the free peptide (I) can be safely ascribed to the exchange of the NH proton with the NH_3^+ group because of their close proximity. Similar behavior can be expected for any NH located in a sufficient spatial proximity with the NH_3^+ group. The smaller T_1^a value for Phe^4 ^{15}N in the free peptide could be explained in that way. Indeed, as shown above $\langle r \rangle = 2.78$ Å for Phe^4 in the free peptide is larger than that for all the other residues while it exhibits the second smaller T_1^a value. This apparent discrepancy may be attributed therefore to an exchange process between Phe^4 NH and the terminal ammonium group. Such a result supports the previously proposed structure[15]—a 1-4 turn that brings into proximity the NH_3^+ group and Phe^4 NH.

The influence of exchange phenomena on ^{15}N relaxation time T_1^a may be analyzed in the following manner: using the Bloch equations modified to include exchange effects, Allerhand and Gutowsky[16] have extensively investigated the decay of the echo amplitude in the Carr–Purcell sequence and this treatment could be directly applied to this ^{15}N modulated proton spin-echo experiment. Nevertheless, without any calculation one may notice that the loss of the spin coherence during the polarization transfer is correlated to ^1H line broadening, which implies a relative mismatch of the echo delay for a large part of the amide protons. The dephasing due to this line broadening is not refocused by the echo sequence. Likewise, an analytical relationship can be derived for calculating the magnetization evolution after the INEPT excitation with the Bloch formalism. However, the small T_1^a of Gly^2 in the free peptide (I) can be interpreted as follows: Since the INEPT sequence results in a selective inversion of only one of the two amide proton doublet signals, the spin-state populations are different for protons coupled to upwards ^{15}N spin and for those coupled to downwards spin. Therefore an exchange with a common set of spins (those of NH_3^+) leads to a loss of specificity of each doublet signal and hence effectively reduces the ^{15}N-induced magnetization as we observed in the case of Tyr-*Gly-*Gly-*Phe.

In 1980 Avent and Freeman[17] proposed a method for obtaining antisymmetric relaxation times. The two essential differences with the experimental scheme proposed here are (i) the use of a pulse sequence without any 90° phase shift in the ^1H excitation and (ii) the introduction of refocusing delays to prevent mutual cancellation of the antiphase component of the spin multiplet during the ^1H noise-decoupled acquisition. Furthermore, their method implies two-dimensional Fourier-transform techniques, requiring rather time-consuming data gathering. This obviously extends the application of this technique to the study of large molecules of biological interest. However, in the case of rather small molecules, our method remains appropriate, because it considerably reduces the number of collected spectra.

In conclusion, the great sensitivity gain of the INEPT sequence is very attractive for relaxation studies which require long instrumental time. This paper demonstrates the usefulness of the cross-polarization method in conformational studies of peptides but also its limitations related to chemical exchange processes. The relaxation times obtained by using this method are not sensitive to the same features as the conventional ones: proton–proton dipolar relaxation and proton-exchange processes are the dominant ^{15}N relaxation mechanisms. At least the distance dependence of the exchange processes between NH_3^+ and NH protons within one peptide makes this sequence suitable for conformational studies of nonprotected linear peptides.

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Effect of Electron Correlation on Theoretical Equilibrium Geometries. 2. Comparison of Third-Order Perturbation and Configuration Interaction Results with Experiment

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Abstract: Theoretical MP3/6-31G* (third-order Møller–Plesset, 6-31G* basis) and CID/6-31G* (configuration interaction with double substitutions, 6-31G* basis) equilibrium geometries have been obtained for a large set of one- and two-heavy-atom molecules containing only first-row elements and for which experimental structural data are available. Both theoretical techniques lead to good agreement with experiment, a majority of the calculated lengths and angles lying within the experimental error range. Systematic bond length deficiencies previously noted at the Hartree–Fock (HF/6-31G*) and second-order Møller–Plesset (MP2/6-31G*) levels are largely removed. Mean absolute differences between MP3/6-31G* theory and experiment are 0.008 Å for bond lengths and 1.3° for bond angles. The MP3/6-31G* and CID/6-31G* methods give comparable results for equilibrium geometries.

Even with quite large basis sets, Hartree–Fock (HF) (single configuration) molecular orbital theory leads to equilibrium structures that show systematic deviations from the best experimental results.[1,2] For a basis such as 6-31G* (split-valence or double-ζ plus polarization functions on non-hydrogen atoms[3]), Hartree–Fock bond lengths are usually too short, particularly for

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[1] Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.

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multiple bonds and single bonds involving electronegative atoms such as oxygen and fluorine.[4,5] These deficiencies are due to neglect of electron correlation; appropriate corrections to the Hartree–Fock treatment have generally improved agreement with experiment.

In a previous paper, an extensive study was made of theoretical equilibrium geometries by using second-order Møller–Plesset (MP) perturbation theory to allow for electron correlation.[6,7] With the 6-31G* basis, this level of theory is denoted by MP2/6-31G*. The MP2 technique is the simplest general method for handling the energy change due to correlation. The set of molecules examined contained all neutral systems with (a) zero, one, or two atoms from the first row (Li to F), (b) any number of hydrogen atoms, and (c) an experimental structure. It was concluded that inclusion of electron correlation at this level did improve the description of equilibrium geometries, although many of the bond lengths became too long rather than too short as at the HF/6-31G* level.

There are many published examples of structure determination, using higher levels of correlation theory, that give excellent agreement with experimental data.[2] For example, studies of diatomic hydrides using CEPA theory by Meyer and Rosmus[8] almost achieve coincidence with the best spectroscopic bond lengths. In the present paper, our objective is to make a systematic study of theoretical performance on equilibrium geometries by using electron correlation techniques better than MP2 but not so complex as to become computationally impractical.

The correlation techniques used here are third-order perturbation theory (MP3)[7c] and configuration interaction with all double substitutions from the Hartree–Fock reference (CID). These techniques are closely related. In a perturbation treatment, CID is correct in third but incorrect in fourth order.[9] At the fourth-order level, CID also has the disadvantage of not being size-consistent. The 6-31G* basis is again employed, so the theoretical models are denoted by MP3/6-31G* and CID/6-31G*. The set of molecules examined contains those with zero, one, or two non-hydrogen atoms (Li to F) and with experimental structures listed in the recent compilations of Huber and Herzberg[10] (diatomics) and Harmony and co-workers[11] (polyatomics).

Our principal objective in this work is to find whether deficiencies noted previously for the MP2/6-31G* method are removed at these higher levels of correlation theory. It should be emphasized, of course, that 6-31G* is not a completely flexible basis, and some variation of predicted geometries with further basis set extension is to be expected. Nevertheless, a systematic comparison of MP2/6-31G* and MP3/6-31G* results should give a fair indication of the role of third-order terms. A secondary objective is a comparison of predictions by MP3 and CID techniques, which should give some indication of the role of the (only partly correct) contributions of double substitutions in higher orders of perturbation theory.

Methods and Results

All computations were carried out by using an extended version of the GAUSSIAN 80 program.[12] The calculations at the MP2 and MP3 levels used the frozen-core approximation (neglect of inner-shell molecular orbitals in correlation calculations) unless otherwise specified. This leads to a significant computational saving. Ditchfield and Seidman[13] have reported MP2/6-31G*-optimized structures of some one-heavy-atom hydrides in which correlation of all electrons is included. Their results do not differ significantly from ours, demonstrating the essential independence of structure on correlation of inner-shell electrons. (A slight exception is Li_2, where inclusion of core-electron correlation reduces MP2 and MP3 bond lengths by about 0.01 Å.)

The MP2 and MP3 structures were obtained by using the Fletcher–Powell minimization algorithm together with first derivatives of the energy obtained by numerical difference.[14a] This technique was also used for some of the smaller CID optimizations (see footnote *d* of Table I). The larger CID/6-31G* structures were obtained by using a similiar algorithm but with analytic first derivatives.[14b,c] Since the analytic derivatives are not easily obtained with the frozen-core approximation, all CID/6-31G* structures allow for correlation of all electrons.

The full set of results is given in Table I, together with the best available experimental values.[15] Most of the HF/6-31G* and MP2/6-31G* geometries were published previously[6] but are included for ease of comparison. The experimental lengths and angles are equilibrium values where known. However, for most polyatomic systems, the anharmonic data required to correct observed average values is not available, and the best values given by Harmony et al.[11] are listed. Part of the deviation between theory and experiment will be due to the absence of such experimental corrections.

Discussion

We first compare the whole set of theoretical results with the experimental data by finding the mean absolute differences for all the independent geometrical parameters evaluated. The results are presented in Table II. These show overall improvement in calculated bond lengths when electron correlation is included but relatively little change in the mean deviation for angles.

For bonds to hydrogen (AH), we have previously noted that adding electron correlation at the MP2 level leads to increased bond lengths and better agreement with experiment. Further progress to MP3 generally leads to an additional lengthening and little change in the overall level of agreement. For the simplest systems (one-heavy-atom molecules AH_n), the MP3/6-31G* lengths are all too long. The largest deviations occur for the polar bonds LiH (too long by 0.047 Å) and FH (too long by 0.015 Å), while the error for CH is only 0.006 Å. These errors are apparently due to the inflexibility of the 6-31G* basis. MP3 bond lengths have been determined with the larger 6-311G** basis[16] and are then LiH = 1.596 Å, CH = 1.124 Å, and FH = 0.909

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Table I. Theoretical and Experimental Structures of One- and Two-Heavy-Atom Molecules[a]

molecule	point group	parameter[b]	HF/6-31G*	MP2/6-31G*[c]	MP3/6-31G*[c]	CID/6-31G*[d]	spectroscopic[e]
H_2	$D_{\infty h}$	r(HH)	0.730	0.738	0.742	0.746	0.741
LiH	$C_{\infty v}$	r(LiH)	1.636	1.640	1.643	1.649	1.596
BeH $^2\Sigma^+$	$C_{\infty v}$	r(BeH)	1.348	1.348	1.351	1.355	1.343
BH	$C_{\infty v}$	r(BH)	1.225	1.234	1.240	1.241	1.232
BH_2 $^2B_1$	C_{2v}	r(BH)	1.185	1.189	1.192	1.193	1.181 C
		∠(HBH)	126.5	127.6	127.8	127.9	131 C
CH $^2\Pi$	$C_{\infty v}$	r(CH)	1.108	1.121	1.126	1.128	1.120
CH_2 $^3B_1$	C_{2v}	r(CH)	1.071	1.078	1.080	1.081	1.078 C
		∠(HCH)	130.4	131.6	131.8	132.0	136 E
CH_3 $^2A_2''$	D_{3h}	r(CH)	1.073	1.079	1.081	1.081	1.079 B
CH_4	T_d	r(CH)	1.084	1.090	1.091	1.091	1.092 A
NH $^3\Sigma^-$	$C_{\infty v}$	r(NH)	1.024	1.039	1.044	1.045	1.036
NH_2 $^2B_1$	C_{2v}	r(NH)	1.013	1.028	1.031	1.030	1.024 C
		∠(HNH)	104.4	103.3	103.2	103.1	103.3 B
NH_3	C_{3v}	r(NH)	1.002	1.017	1.017	1.016	1.012 B
		∠(HNH)	107.2	106.3	106.2	106.3	106.7 B
OH $^2\Pi$	$C_{\infty v}$	r(OH)	0.959	0.979	0.981	0.980	0.970
OH_2	C_{2v}	r(OH)	0.947	0.969	0.967	0.966	0.958 A
		∠(HOH)	105.5	104.0	104.3	104.3	104.5 A
FH	$C_{\infty v}$	r(FH)	0.911	0.934	0.932	0.931	0.917
Li_2	$D_{\infty h}$	r(LiLi)	2.812	2.782[f]	2.760[g]	2.724	2.673
LiF	$C_{\infty v}$	r(LiF)	1.555	1.570	1.565	1.562	1.564
B_2H_6	D_{2h}	r(BB)	1.778	1.754	1.753	1.750	1.763 C
		$r(\mathrm{BH_t})$	1.185	1.190	1.192	1.190	1.201 C
		$r(\mathrm{BH_b})$	1.316	1.311	1.312	1.310	1.320 C
		$\angle(\mathrm{H_tBH_t})$	122.1	121.7	121.6	121.5	121.0 C
BO $^2\Sigma^+$	$C_{\infty v}$	r(BO)	1.187	1.218	1.204	1.203	1.204
BN $^3\Pi$	$C_{\infty v}$	r(BN)	1.293	1.327	1.276	1.287	1.281
BF	$C_{\infty v}$	r(BF)	1.261	1.281	1.276	1.274	1.263
C_2 $^1\Sigma_g^+$	$D_{\infty h}$	r(CC)	1.245	1.265	1.237	1.244	1.243
C_2H_2	$D_{\infty h}$	r(CC)	1.185	1.218	1.206	1.202	1.203 A
		r(CH)	1.057	1.066	1.066	1.065	1.061 A
C_2H_4	D_{2h}	r(CC)	1.317	1.336	1.334	1.328	1.339 B
		r(CH)	1.076	1.085	1.086	1.084	1.085 B
		∠(HCH)	116.4	116.6	116.4	116.3	117.8 B
HCN	$C_{\infty v}$	r(CN)	1.133	1.177	1.158	1.154	1.153 A
		r(CH)	1.059	1.070	1.067	1.067	1.065 A
HNC	$C_{\infty v}$	r(CN)	1.154	1.187	1.174	1.171	1.172 B
		r(NH)	0.985	1.002	1.000	0.997	0.986 B
CH_2NH	C_s	r(CN)	1.250	1.282	1.275	1.268	1.273 C
		r(NH)	1.006	1.027	1.025	1.021	1.023 D
		$r(\mathrm{CH_c})$	1.084	1.096	1.095	1.092	1.103 D
		$r(\mathrm{CH_t})$	1.080	1.090	1.090	1.087	1.081 D
		∠(HNC)	111.6	109.7	110.1	110.4	110.5 E
		$\angle(\mathrm{NCH_c})$	124.7	125.4	125.2	125.1	123.4 X
		∠(HCH)	116.1	116.1	116.1	116.1	116.9 C
CH_3NH_2	C_s	r(CN)	1.453	1.465	1.466	1.460	1.471 C
		$r(\mathrm{CH_i})$	1.091	1.100	1.101	1.098	1.099 D
		$r(\mathrm{CH_o})$	1.084	1.092	1.093	1.091	
		r(NH)	1.001	1.018	1.018	1.014	1.010 D
		∠(HNC)	110.7	109.5	109.5	109.8	110.3 D
		∠(HNH)	106.9	105.9	105.9	106.1	107.1 D
		$\angle(\mathrm{H_iCN})$	114.8	115.4	115.2	115.2	113.9 D
		$\angle(\mathrm{H_{oo}CN})$	123.9	123.7	123.2	123.4	124.4 D
		$\angle(\mathrm{H_oCH_o})$	107.5	107.5	107.5	107.4	108.0 D
CO	$C_{\infty v}$	r(CO)	1.114	1.151	1.135	1.133	1.128
H_2CO	C_{2v}	r(CO)	1.184	1.221	1.210	1.205	1.208 B
		r(CH)	1.092	1.104	1.104	1.101	1.116 C
		∠(HCH)	115.7	115.6	116.0	115.8	116.5 C
CH_3OH	C_s	r(CO)	1.400	1.424	1.421	1.415	1.421 A
		$r(\mathrm{CH_i})$	1.081	1.090	1.091	1.088	1.094 B
		$r(\mathrm{CH_o})$	1.087	1.097	1.098	1.095	
		r(OH)	0.946	0.970	0.967	0.963	0.963 C
		∠(HOC)	109.4	107.4	107.7	108.1	108.0 B
		$\angle(\mathrm{H_iCO})$	107.2	106.4	106.4	106.6	107.2 B
		$\angle(\mathrm{H_{oo}CO})$	130.1	130.7	130.5	130.4	129.9 B
		$\angle(\mathrm{H_oCH_o})$	108.7	108.7	108.8	108.8	108.5 B
CF $^2\Pi$	$C_{\infty v}$	r(CF)	1.267	1.290	1.284	1.284	1.272
CH_3F	C_{3v}	r(CF)	1.365	1.392	1.388	1.382	1.383 A
		r(CH)	1.082	1.092	1.093	1.090	1.100 B
		∠(HCH)	109.8	109.8	109.9	109.8	110.6 B
N_2	$D_{\infty h}$	r(NN)	1.078	1.131	1.116	1.103	1.098
N_2H_2	C_{2h}	r(NN)	1.216	1.267	1.250	1.242	1.252 B
		r(NH)	1.014	1.036	1.035	1.031	1.028 C
		∠(HNN)	107.5	105.4	106.1	106.4	106.9 C
N_2H_4	C_2	r(NN)	1.413	1.439	1.440	1.430	1.447 B

Table I (*Continued*)

molecule	point group	parameter[b]	HF/6-31G*	MP2/6-31G*[c]	MP3/6-31G*[c]	CID/6-31G*[d]	spectroscopic[e]
		$r(NH_a)$	0.999	1.016	1.016	1.012	1.008 D
		$r(NH_b)$	1.003	1.021	1.020	1.016	
		$\angle(H_aNN)$	107.9	106.3	106.3	106.8	109.2 D
		$\angle(H_bNN)$	112.3	111.5	111.3	111.6	
		$\angle(H_aNH_b)$	108.2	107.0	106.9	107.2	113.3 D
		$\omega(H_aNNH_b)$	90.2	90.5	90.9	90.8	88.9 D
HNO	C_s	$r(NO)$	1.175	1.237	1.213	1.206	1.212 A
		$r(NH)$	1.032	1.058	1.057	1.052	1.063 C
		$\angle(HNO)$	108.8	107.3	107.9	108.0	108.6 B
H_2NOH	C_s	$r(NO)$	1.403	1.453	1.444	1.433	1.453 B
		$r(NH)$	1.002	1.021	1.020	1.016	1.016 C
		$r(OH)$	0.946	0.971	0.968	0.964	0.962 D
		$\angle(HNH)$	106.5	105.2	105.3	105.6	107.1 D
		$\angle(HNO)$	104.8	102.8	103.2	102.5	103.2 C
		$\angle(NOH)$	104.2	101.2	102.0	103.6	101.4 D
NF $^3\Sigma^-$	$C_{\infty v}$	$r(NF)$	1.302	1.330	1.327	1.324	1.317
O_2 $^3\Sigma_g^-$	$D_{\infty h}$	$r(OO)$	1.168	1.247	1.211	1.206	1.208
HOF	C_s	$r(OF)$	1.376	1.444	1.433	1.420	1.442 B
		$r(OH)$	0.952	0.979	0.975	0.971	0.966 D
		$\angle(HOF)$	99.8	97.2	98.0	98.3	96.8 C
F_2	$D_{\infty h}$	$r(FF)$	1.345	1.421	1.415	1.399	1.412

[a] Angles in degrees, distances in angstroms. Most of the HF and MP2 parameters appear in ref 6. [b] Subscripts used on hydrogen atoms: H_b, H_t, bridging and terminal hydrogens in B_2H_6; H_c, H_t, hydrogens cis and trans to imino hydrogen in CH_2NH; H_i, H_o, in- and out-of-plane hydrogens in CH_3NH_2 and CH_3OH; H_{oo} is the bisector of the equivalent out-of-plane hydrogens in CH_3NH_2 and CH_3OH; H_a, H_b, to distinguish inequivalent hydrogens in N_2H_4. [c] The frozen-core approximation is utilized for all entries. [d] The frozen-core approximation is utilized only for CH, OH, NH, BeH, BH_2, CH_2, CH_3, O_2, NF, NH_2, and CF. [e] Diatomic data from ref 10, all other values are from ref 11. Letter symbols for uncertainty interpreted in ref 11. [f] Inclusion of inner-shell correlation decreases this value to 2.773. [g] Inclusion of inner-shell correlation decreases this value to 2.750.

Table II. Mean Absolute Deviations between Theoretical and Experimental Geometrical Parameters[a, b]

type	no. of comparisons	HF	MP2	MP3	CID
AH bond lengths	39	0.012	0.009	0.008	0.007
AB bond lengths	27	0.028	0.023	0.009	0.009
all bond lengths	66	0.018	0.014	0.008	0.008
angles	31	1.4	1.4	1.3	1.3

[a] Using the 6-31G* basis. [b] Bond lengths in angstroms, angles (including dihedral angles) in degrees.

Å, all in close agreement with the experimental values. A similar effect is found for the OH bond in water, which is reduced to 0.954 Å at the MP3/6-311G** level. The CID/6-31G* bond lengths to hydrogen parallel the MP3 values closely and have similar deficiencies.

Bond lengths between non-hydrogen atoms (AB) are more strongly changed by inclusion of electron correlation. For the standard single, double, and triple bonds connecting carbon, nitrogen, oxygen, and fluorine (Table III), HF/6-31G* lengths are all too short. When electron correlation is included at the MP2/6-31G* level, all bond lengths increase and become mostly longer than experimental values. Further progress to MP3/6-31G* leads to a reduction to values that cluster closely about the experimental results. The overcorrection of bond lengths at the MP2 level is particularly marked for multiple bonds.

Molecular lithium, Li_2, shows the greatest error of all calculated bond lengths in Table I. The large error of 0.139 Å at HF/6-31G* is partly corrected when electron correlation is introduced, but the large residual discrepancy is principally due to basis-set limitation. Li_2 bond lengths with the 6-311G** basis are 2.785 (HF), 2.749 (MP2), 2.725 (MP3), and 2.693 (CID). These values are closer to the experimental result of 2.637 Å. The other AB diatomics listed in Table I behave similarly to the standard bonds of Table II. Most lengths are too short at the Hartree–Fock level; all become longer than experiment at MP2/6-31G*. On going further to MP3/6-31G*, some shortening occurs, leading to reasonable overall agreement with experiment. The behavior of carbon monoxide (too short by 0.014 Å at HF, too long by 0.023 Å at MP2, and too long by 0.005Å at MP3) is typical.

Table III. Deviations[a] (Theory – Experiment) for Standard Single, Double, and Triple Bonds

bond	HF	MP2	MP3
C–N	−18	−6	−5
C–O	−21	+3	0
C–F	−18	+9	+5
N–N	−34	−8	−7
N–O	−50	0	−9
O–F	−66	+2	−9
F–F	−67	+9	−13
C=C	−22	−3	−5
C=N	−23	+9	+2
C=O	−24	+13	+2
N=N	−36	+15	−2
N=O	−37	+25	+1
O=O	−40	+39	+3
C≡C	−18	+15	+3
C≡N	−20	+24	+5
N≡N	−20	+33	+18

[a] Units of 10^{-11} cm.

The overall statistical results (Table II) show only a slight, hardly significant, improvement in the description of bond angles when correlation is included at the MP2, MP3, or CID levels. It may be noted that the greatest deviations occur in systems in which the experimental determination is somewhat imprecise, such as the HCH angle in triplet methylene and the HNH angle in hydrazine. There are considerable difficulties in extracting accurate equilibrium angles from rotational energy levels; the partition of the remaining deviation into theoretical and experimental error remains uncertain.

It is of interest to compare predictions at the two highest levels of theory, MP3/6-31G* and CID/6-31G*. For the 66 independent bond lengths listed in Table I, the mean absolute difference between the two predictions is 0.005 Å. This is substantially less than the mean deviation of either from experiment (Table II). For the 31 independent angles, the corresponding mean absolute difference is a negligible 0.2°. We conclude that these two techniques give comparable results for equilibrium structures.[17]

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(17) Unpublished studies (by DJD) on AH_n systems using the 6-31G* basis set indicate that extension of configuration interaction to include single substitutions (CISD) has an insignificant effect on computed geometries.

One final comparison with experiment may be made. The polyatomic spectroscopic tabulation of Harmony et al. includes estimated error ranges (symbols A-E in Table I). For example, the symbol C attached to a bond length implies an error range of ±0.005 to ±0.01 Å. If we take the larger error estimate in each case, then 54 out of the 75 parameters (72%) so assessed (Table I) are calculated within the experimental range at the MP3/6-31G* level.

Conclusions

(1) For the wide range of molecules examined, MP3/6-31G* and CID/6-31G* equilibrium geometries are in good agreement with experimental data. A majority of the calculated lengths and angles lie within the error range associated with the experimental data.

(2) Systematic bond length deficiencies at HF/6-31G* (theory too short) and at MP2/6-31G* (theory too long) are largely removed at the third-order level.

(3) Equilibrium geometries predicted by Møller-Plesset (MP3) and configuration interaction (CID) techniques are close.

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Registry No. H_2, 1333-74-0; LiH, 7580-67-8; BeH, 13597-97-2; BH, 13766-26-2; BH_2, 14452-64-3; CH, 3315-37-5; CH_2, 2465-56-7; CH_3, 2229-07-4; CH_4, 74-82-8; NH, 13774-92-0; NH_2, 13770-40-6; NH_3, 7664-41-7; OH, 3352-57-6; OH_2, 7732-18-5; FH, 7664-39-3; Li_2, 14452-59-6; LiF, 7789-24-4; B_2H_6, 19287-45-7; BiO, 12505-77-0; BN, 10043-11-5; BF, 7637-07-2; C_2, 12070-15-4; C_2H_2, 74-86-2; C_2H_4, 74-85-1; HCN, 74-90-8; HNC, 6914-07-4; CH_2NH, 2053-29-4; CH_3NH_2, 74-89-5; CO, 630-08-0; H_2CO, 50-00-0; CH_3OH, 67-56-1; CF, 3889-75-6; CH_3F, 593-53-3; N_2, 7727-37-9; N_2H_2, 3618-65-1; N_2H_4, 302-01-2; NHO, 14332-28-6; H_2NOH, 7803-49-8; NF, 13967-06-1; O_2, 7782-44-7; HOF, 14034-79-8; F_2, 7782-41-4.

Metal Ion Photoinitiated Addition of Acetonitrile and Methanol to Olefins

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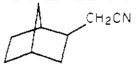
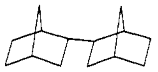
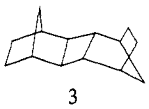
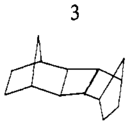
Abstract: Irradiation of norbornene and silver or thallium trifluoromethanesulfonate in acetonitrile solution results in the efficient formation of *exo*-2-(cyanomethyl)bicyclo[2.2.1]heptane. Investigation of the scope of this reaction established that (a) copper(I or II) salts are not effective, (b) propionitrile and methanol give analogous norbornene-solvent adducts, and (c) acetonitrile addition is observed for several cyclic and acyclic olefins. Investigation of the mechanism of solvent addition indicates that the reaction is initiated by photoinduced electron transfer to silver(I) from coordinated norbornene. Reaction of the resulting norbornene cation radical with acetonitrile yields norbornyl cation and cyanomethyl radical. Free-radical chain addition of the cyanomethyl radical to norbornene then leads to product formation. In ethereal solvents, metal ion catalyzed photodimerization of norbornene has previously been reported for copper(I) salts. This reaction can also be effected by copper(II) and silver(I) salts, but not by Tl(I) salts.

Copper(I) salts are effective photocatalysts for olefin isomerization and cycloaddition reactions.[1] Among the most extensively investigated of these reactions is the photodimerization of norbornene to yield predominantly the exo-trans-exo dimer, a reaction first described by Trecker and co-workers.[2] The structure and bonding in Cu(I)-olefin complexes and the mechanism of photodimerization were subsequently investigated in detail by Salomon and Kochi.[3] In contrast to the extensive investigations of Cu(I)-olefin photochemical reactions, there is but a single report of Ag(I)-assisted photodimerization[4] and no reports of Tl(I)- or Cu(II)-olefin photochemistry. In addition, the effects of solvents on metal ion-olefin photochemistry have not been studied. We have investigated and report here the photochemical behavior of norbornene in the presence of Cu(I), Ag(I), Tl(I), and Cu(II) triflates in several solvents.[5] In addition to the previously reported photocatalyzed dimerization of norbornene,[1] a novel and efficient photoinitiated free-radical chain addition of solvent (acetonitrile and methanol) to norbornene and other olefins is observed and its mechanism elucidated. It is seen that the intrinsic coordinative preferences of the different metal ions profoundly influence the course and efficiency of the photochemical reactions.

Table I. Percent Yields of Photoproducts from Norbornene in Acetonitrile

	AgOTf initiated[a]		xylene sensitized[b]	
product	CH_3CN	CD_3CN	CH_3CN	CD_3CN
 1	93 ± 3[c]	23 (d_3)	86	18
 **2**	3 ± 0.5	38 (d_2)	9	18
 3	1 ± 0.5	12 (d_0)	1	8
 4	3 ± 0.5	27 (d_0)	4	56

[a] Percent yields determined by gas chromatography at ca. 1% conversion of norbornene (0.25 m) and AgOTf (0.02 m). [b] Reference 6. [c] Deviations in percent yield are typical of the data in Tables I and V.

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