Table IX. ^{31}P NMR Data[a] for Phosphino–Diphosphanes $(^iPr_2N)_2P_A—P_B=P_C—R$ (**8a–g**)

R	$\delta(^{31}P)$, ppm			J_{PP}, Hz		
	P_A	P_B	P_C	P_AP_B	P_BP_C	P_AP_C
Mes*	70.4	502.7	554.0	181	574	403
$^iPr_2N$	61.7	245.7	483.9	197	534	541
$Me_3Si_2N(Me_3Si)N$	60.8	298.7	522.3	186	522	505
$(-Me_2C(CH_2)_3CMe_2-)N$	73.7	320.1	496.5	205	574	603
Mes*(H)N	61.4	407.4	544.0	174	570	609
$(Me_2Bu^tSi)_2N$	67.9	442.9	577.6	190	602	566
Mes*O	53.9	386.2	590.2	169	564	601

[a] All values are given relative to H_3PO_4. Positive values designate downfield chemical shifts.

opposite is observed for the PP double-bond lengths (2.03 Å, **8d**; 2.01 Å, **8f**). The bond lengths and bond angles for the $P(N^iPr_2)_2$ ligand are quite normal. However, in the phosphino–diphosphenes the P(1)–P(2)–P(3) angle is smaller; it even decreases in the series **8a** > **8f** > **8d** below 90°!

d. NMR Studies. The ^{31}P NMR data for compounds **8a–g** are given in Table IX. All compounds give 12 lines according to an AMX pattern (three doublets of doublets). The resonances at high fields (δ 54–74 ppm) are due to the phosphino group while those at lower fields are indicative of the PP double-bond system.[1a] Note that the shift at the nucleus P_B shows a significant correlation with the "nature" of the ligand R. It can be interpreted in terms of the π-donating ability of the ligand. In the series of the amino-substituted derivatives **8b–g** the signal is shifted from 443 ppm for **8f** (with an almost orthogonal arrangement of the NSi_2 group with respect to the central π system) to 246 ppm for **8b**, which adopts a coplanar conformation. In the case of **8d** (δ 320 ppm) the nitrogen ligand is twisted by 12° out of the NPP plane. A similar trend in $\delta(^{31}P)$ is observed for the nucleus P_A, but to a smaller extent. The values for the $^1J_{P(B)P(C)}$ coupling constant (534–602 Hz) are similar to those observed for asymmetric substituted diphosphenes. However, the most remarkable features of all phosphino–diphosphenes are the large two-bond coupling constants $^2J_{P(A)P(C)}$ (400–600 Hz), which are in some cases larger than the values found for the interaction of the double-bond system in the same molecule (**8b,d,e,g**).

As has been shown by X-ray data analysis for **8a,d,f**, the two phosphorus lone pairs are nearly in the same plane. This special conformation combined with the small angle $P_aP_BP_C$ involves enhancement of $^2J_{P(B)P(C)}$.

Conclusions

The results of our investigations can be summarized as follows.

(1) According to quantum-chemical calculations an electronegative substituent at the PP double bond causes the formation of the close ion pair X^-PPH^+. Concomitantly, unusual structures are predicted that depart from the conventional picture of known double-bond systems. The β-phosphorus atom tends to adopt an umbrella conformation, i.e. a bridged structure.

(2) The theoretical predictions are fully confirmed by structural investigations on a selected variety of substituted diaminophosphino–diphosphenes, which were synthesized for this purpose. These structures are the first ones toward a realization of bridged structures in the chemistry of multiple bonding between heavier main-group elements.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were performed on a Cyber 205 computer (Ruhr-Universität Bochum). We thank Udo Welz for computational assistance.

Registry No. *cis*-**1** (R^α = H, R^β = H), 87678-58-8; *trans*-**1** (R^α = H, R^β = H), 87678-57-7; *cis*-**1** (R^α = F, R^β = H), 122049-31-4; *trans*-**1** (R^α = F, R^β = H), 122049-48-3; *cis*-**1** (R^α = Cl, R^β = H), 122049-32-5; *trans*-**1** (R^α = Cl, R^β = H), 122049-49-4; *cis*-**1** (R^α = OH, R^β = H), 122049-33-6; *trans*-**1** (R^α = OH, R^β = H), 122049-50-7; *cis*-**1** (R^α = NH_2, R^β = H), 122049-41-6; *trans*-**1** (R^α = NH_2, R^β = H), 122049-51-8; *cis*-**1** (R^α = CH_3, R^β = H), 122049-42-7; *trans*-**1** (R^α = CH_3, R^β = H), 122049-52-9; *cis*-**1** (R^α = SiH_3, R^β = H), 122049-43-8; *trans*-**1** (R^α = SiH_3, R^β = H), 122049-53-0; **2**, 117270-09-4; **3**, 91443-42-4; **5**, 54043-94-6; **6c**, 111437-98-0; **6d**, 64945-24-0; **6e**, 122049-47-2; **6f**, 85909-11-1; **6g**, 796-62-3; **8a**, 122049-34-7; **8b**, 122049-35-8; **8c**, 122049-36-9; **8d**, 122049-37-0; **8e**, 122049-38-1; **8f**, 122049-39-2; **8g**, 122049-40-5; **9b**, 122049-45-0; $(i-Pr_2N)_2PP(Cl)P(SiMe_3)Mes^*$, 122049-30-3; P_2H^+ (cyclic), 122049-44-9; $(i-Pr_2N)_2PP(Li)SiMe_3$, 122049-46-1; P_2H^+ (linear), 12339-20-7.

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Molecular Structure and Internal Rotation Potential of Perfluoro-2,3-diaza-1,3-butadiene, $CF_2=N—N=CF_2$. An Electron Diffraction and ab Initio Study

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A gas-phase electron diffraction study of perfluoro-2,3-diaza-1,3-butadiene results in a planar trans structure with the following geometric parameters (r_a values with 3σ uncertainties): N—N = 1.421 (12), C=N = 1.264 (7), C—F = 1.304 (4) Å; N—N=C = 112.7 (9), F—C—F = 110.8 (9)°. The CF_2 groups are tilted by 5.0 (8)° toward the nitrogen lone pairs. No additional conformer has been observed. Ab initio calculations for $CH_2=N—N=CH_2$ (6-31G** basis) and $CF_2=N—N=CF_2$ (6-31G* basis) demonstrate that the internal rotation potentials change drastically if electron correlation is included at the MP2 level. Whereas SCF-HF calculations predict the planar trans forms to be the only stable conformers, the MP2 method predicts additional high-energy gauche conformers with ΔE = 0.8 ($CH_2=N—N=CH_2$) and 1.8 kcal mol^{-1} ($CF_2=N—N=CF_2$). Both values are in good agreement with experiment, ΔE = 1.2 (5) kcal mol^{-1} for the parent compound and $\Delta G \geq 1.8$ kcal mol^{-1} for the fluorinated species.

Introduction

Structure and conformational properties of the simplest conjugated systems, 1,3-butadiene and the isoelectronic glyoxal, have attracted considerable interest over the past decades. It is well established by experimental methods (electron diffraction,[1] vibrational spectroscopy[2]) and by ab initio calculations[3,4] that the

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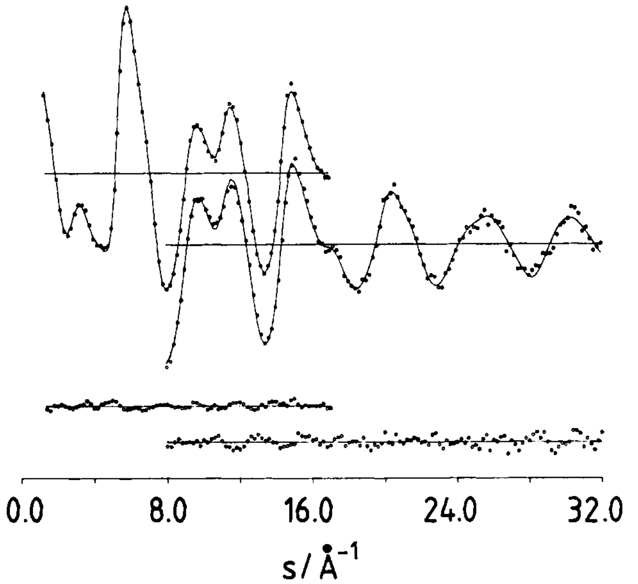

Figure 1. Experimental (ooo) and calculated (—) molecular intensities and differences.

most stable conformer of 1,3-butadiene is the planar trans form and the less stable conformer has a cis-gauche structure. From calorimetric[5] and spectroscopic data[2,6] an energy difference between 2.1 and 3.1 kcal mol^{-1} is estimated in good agreement with high-quality ab initio calculations,[3] which predict 3.15 kcal mol^{-1}. Glyoxal experimental studies (electronic[7,8] and microwave spectra[9]) and ab initio calculations[10] find a high-energy planar cis conformer beside the most stable planar trans structure.[11] For this compound experimental values for the energy difference of 3.2 (6) and 3.8 (6) kcal mol^{-1} have been reported,[7,12] and ab initio calculations predict values of 5.86,[11a] 5.6,[11b] 5.1,[11c] and 4.25 kcal mol^{-1}.[11d] An electron diffraction study[13] for the isoelectronic 2,3-diaza-1,3-butadiene (formaldazine), $CH_2=N-N=CH_2$, which was carried out at temperatures between −30 and +225 °C, results in a mixture of trans and cis-gauche conformers with an energy difference of 1.2 (5) kcal mol^{-1}. The existence of a second high-energy conformer is confirmed by matrix IR spectra.[14]

Fluorination has a drastic effect on the conformation of 1,3-butadiene. Gas-phase electron diffraction[15] and photoelectron and optical spectra[16] demonstrate that in perfluoro-1,3-butadiene the cis-gauche conformation is the most stable structure and no contribution of the planar trans conformer has been observed. This experimental observation has recently been reproduced correctly by ab initio calculations that predict the planar trans conformation to be higher in energy by 1.8 kcal mol^{-1} relative to the gauche structure.[17] IR and Raman spectra[18] and electron diffraction intensities[19] for oxalyl fluoride, $(COF)_2$, are interpreted as a mixture of planar trans and cis conformers in the gas phase, with the trans form favored but indicating that the energy difference between these two conformations is lowered appreciably upon fluorination. This has been confirmed by ab initio calculations that predict the cis form to be higher in energy by only 0.54 kcal mol^{-1} (4-31G basis) or 0.13 kcal mol^{-1} (STO-4G basis) than the trans conformer.[20]

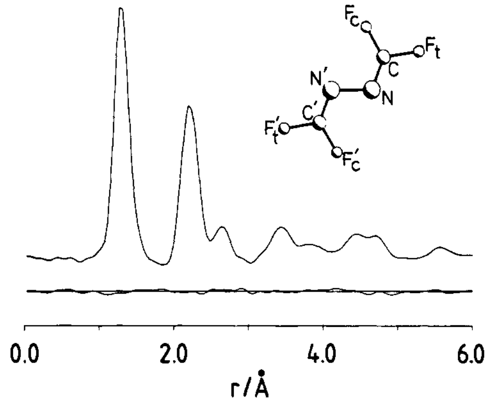

Figure 2. Experimental radial distribution function and difference curve.

Table I. Results of Electron Diffraction Analysis for $CF_2=N-N=CF_2$

(a) Geometric Parameters[a]

C=N	1.264 (7)	F—C—F	110.8 (9)
C—F	1.304 (4)	tilt[b]	5.0 (8)
N—N	1.421 (12)	$(CNNC)_{eff}$	153 (5)
N—N=C	112.7 (9)		

(b) Interatomic Distances and Vibrational Amplitudes

C=N	1.26	0.040[c]	C···C′	3.30	0.070[c]
C—F	1.30	0.046 (6)	N···F_t′	3.47	0.084 (16)
N—N	1.42	0.050[c]	C···F_c′	3.84	0.16 (5)
F_c···F_t	2.15	0.056 (10)	C···F_t′	4.41	0.09 (3)
N···C′	2.24		F_c···F_c′	4.67	0.15 (3)
N···F_t	2.22	0.073 (9)	F_c···F_t′	4.70	
N···F_c	2.32		F_t···F_t′	5.61	0.11 (5)
N···F_c′	2.66				

(c) Agreement Factors for the Two Camera Distances[d]

$R_{50} = 0.039$ $R_{25} = 0.134$

[a] r_a values in angstroms and degrees. Estimated uncertainties are 3σ values and include systematic errors (see text). [b] Tilt angle of CF_2 group toward nitrogen lone pair. [c] Not refined. [d] $R = [\sum w_i\Delta_i^2/\sum w_i(s_iM_i^{expt})^2]^{1/2}$; $\Delta_i = s_iM_i^{expt} - s_iM_i^{calc}$; w_i = weight.

The first synthesis of the perfluorinated species of 2,3-diaza-1,3-butadiene has been reported by Mitsch.[21] The IR (gas) and Raman (liquid) spectra were interpreted in terms of a planar trans configuration.[22] In this study we report a structure determination of $CF_2=N-N=CF_2$ by gas electron diffraction with special attention to the possible presence of a second conformer. For further elucidation of the effect of fluorination on the shape of the internal rotation potential, we perform ab initio calculations for $CH_2=N-N=CH_2$ and its perfluorinated species.

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Table II. HF-Optimized Geometries (Å, deg) for $H_2C{=}N{-}N{=}CH_2$ at Various CNNC Dihedral Angles (deg) and Relative HF Energies (ΔE_{HF}^{HF}) and MP2 Energies (kcal mol^{-1}) at HF Geometries (ΔE_{HF}^{MP}) and MP2 Geometries (ΔE_{MP}^{MP})

CNNC	N—N	N=C	C—H$_t$	C—H$_c$	NNC	HCH	tilt[a]	ΔE_{HF}^{HF}[b]	ΔE_{HF}^{MP}[c]	ΔE_{MP}^{MP}[d]
cis	1.411	1.251	1.077	1.081	122.3	116.7	4.7	16.61	14.87	14.70
30	1.386	1.253	1.076	1.082	120.5	117.8	3.5	11.23		
60	1.369	1.252	1.076	1.082	118.3	118.8	2.5	5.18	1.92	2.03
75	1.368	1.251	1.076	1.082	117.8	118.7	2.4	4.02	0.89	1.06
90	1.370	1.250	1.076	1.082	117.3	118.7	2.4	3.54	0.65	0.86
105	1.375	1.250	1.076	1.081	116.3	118.7	2.4	3.20	0.72	
120	1.383	1.250	1.076	1.081	115.0	118.8	2.4	2.64	0.74	0.90
150	1.392	1.252	1.076	1.080	113.0	119.0	2.2	0.90		
trans	1.396	1.253	1.076	1.080	112.3	119.2	2.1	0.00	0.00	0.00

[a] Tilt angle of CH_2 group toward nitrogen lone pair. [b] $E_t = -186.8928674$ au. [c] $E_t = -187.4850115$ au. [d] $E_t = -187.4885068$ au; all E_t values at the trans configuration.

Experimental Section

$CF_2{=}N{-}N{=}CF_2$ was prepared by the low-pressure pyrolysis of $CF_2{=}N{-}Br$ at 550 °C.[23] The IR spectra at 10 and 100 Torr indicated no impurities.

The electron diffraction intensities were recorded with the Balzers KD-G2 gas diffractograph[24] at two camera distances (25 and 50 cm). The electron wavelength (ca. 60 kV accelerating voltage) was calibrated with ZnO diffraction patterns. The sample reservoir was kept at −53 °C, and the stainless steel inlet system and nozzle were at room temperature. The camera pressure never exceeded 10^{-5} Torr during the experiment. Due to the very small amount of sample available, only two photographic plates (Kodak Electron Image plates, 13 × 18 cm) could be exposed at each camera distance. Both short-distance plates were rather light (optical densities below 0.1), which makes the intensities for this s range more noisy than usual. The four plates were evaluated by the usual procedures,[25] and the averaged molecular intensities in the s ranges 1.4–17 and 8–32 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 1.

Structure Analysis for $CF_2{=}N{-}N{=}CF_2$. The radial distribution curve (Figure 2) was calculated with an artificial damping constant of 0.002 Å^2. The geometric structure of the planar trans configuration is characterized by three bond lengths (N—N, N=C, C—F), two bond angles (NNC, FCF), and a tilt angle between the FCF bisector and the N=C bond direction (tilt in the molecular plane; positive values imply tilt toward nitrogen lone pair). Preliminary structure refinements indicated that an effective dihedral angle[26] $(CNNC)_{eff} < 180°$ had to be introduced as an additional parameter in order to account for the large amplitude torsional vibration around the N—N bond. The vibrational amplitudes for the N—N and N=C distances had to be constrained in the least-squares analyses. Further assumptions for the vibrational amplitudes are evident from Table I. With these constraints seven geometric parameters and nine vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$: NC/CF = −0.94, CF/FCF = −0.61, NNC/tilt = −0.64, CF/l(CF) = −0.86, and NC/l(CF) = 0.89. The molecular intensities were modified with a diagonal weight function,[25] and scattering amplitudes and phases of Haase[27] were used in the least-squares analyses. The final results are summarized in Table I. Estimated uncertainties are based on 3σ values and include possible systematic errors due to the assumptions made for bonded vibrational amplitudes. These contributions were estimated by varying the values for the N—N and N=C amplitudes by ±0.005 Å.

Model calculations demonstrate that the molecular intensities at small scattering angels and the radial distribution curve in the region of long nonbonded distances are very sensitive toward small contributions from a cis-gauche conformer. Such a structure is characterized by several nonbonded C···F and F···F distances around 4 Å, where no distances in the trans conformer occur, and by no distances in the region $4.2 < r < 5$ Å, where several distances in the trans conformer occur. A series of least-squares analyses with various but fixed contributions of the gauche conformer were performed. The bond lengths and angles for the gauche conformer were constrained to the values for the trans form, except for the NNC angle, which was increased according to the ab initio calculations (see below). The CNNC dihedral angle was varied from 60 to 100°. The agreement factor for the long camera distance data, R_{50}, increased in all these analyses, and we estimate an upper limit of 10% gauche contribution, which leads to an increase of R_{50} by 20%. This corresponds to a lower limit of 1.8 kcal mol^{-1} for the free enthalpy difference between gauche and trans conformers.

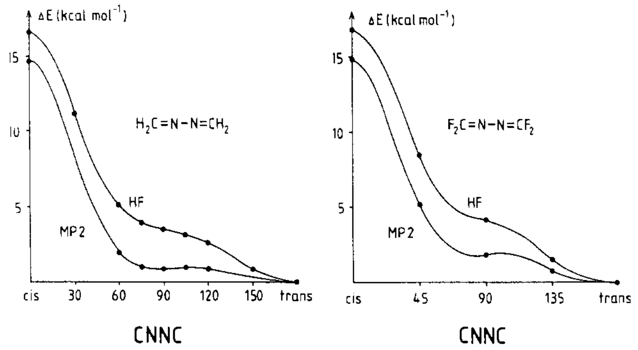

Figure 3. Calculated internal rotation potentials at HF and MP2 approximations.

Ab Initio Calculations

The shapes of the potentials for internal rotation in 1,3-butadiene[4] and glyoxal[10] have been studied repeatedly in great detail by ab initio methods. Less sophisticated calculations in the HF approximation using split valence basis sets without polarization functions have been reported for the isoelectronic 2,3-diaza-1,3-butadiene.[28] If the experimental geometries are used, a potential with a single minimum at the trans position is predicted. The experimental findings, i.e. a second higher energy gauche conformer, are reproduced qualitatively with partial adjustment of the geometry. This gauche conformation at CNNC ≈ 80° lies 3.5 kcal mol^{-1} above the trans structure. Since we were interested in the effect of fluorination on the internal rotation potential, we performed calculations for the parent diaza compound and for the perfluorinated species. The program suite GAUSSIAN 82[29] and double-ζ basis sets with polarization functions (6-31G**) were used.

2,3-Diaza-1,3-butadiene. Geometries were fully optimized by HF gradient methods for various CNNC dihedral angles between 0 (cis) and 180° (trans) in steps of 30°. Two additional points at 75 and 105° were included. The geometric parameters and relative HF energies (ΔE_{HF}^{HF}) are summarized in Table II. Deviations of the CH_2 groups from coplanarity with the NNC plane are minor and are not given in the table. The torsional potential is displayed in Figure 3 (curve HF). At the HF level the potential for internal rotation has a shoulder around the 90° dihedral angle and 3.5 kcal mol^{-1} above the trans conformation but no second minimum. This is in direct conflict with the experiments,[13,14] and therefore, further calculations that go beyond the HF level were performed. The relative energies obtained in second-order Moller–Plesset approximation (MP2)[30] for the HF-optimized geometries (ΔE_{HF}^{MP}) are also listed in Table II. This internal rotation potential (not displayed in Figure 3) has a very flat second minimum at a dihedral angle near 90°, about 0.6 kcal mol^{-1} above the trans structure.

Since HF calculations with 6-31G** basis sets are known to result in too short bond lengths, which may have a small but in our case significant influence on the internal rotation potential, we estimated this effect by optimizing the skeletal parameters (N—N, N=C, NNC) for the trans configuration at the MP2 level. Inclusion of electron correlation lengthens the N—N and N=C bonds by about 0.03 and 0.04 Å and

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Table III. HF-Optimized Geometries (Å, deg) for $F_2C{=}N{-}N{=}CF_2$ at Various CNNC Dihedral Angles (deg) and Relative HF Energies (ΔE^{HF}_{HF}) and MP2 Energies (kcal mol^{-1}) at MP2-Adjusted Geometries (ΔE^{MP}_{MP})

CNNR	N—N	N=C	C—F$_t$	C—F$_c$	NNC	FCF	tilt[a]	ΔE^{HF}_{HF}[b]	ΔE^{MP}_{MP}[c]
cis	1.376	1.231	1.290	1.293	128.8	108.9	5.4	16.71	14.74
45	1.378	1.231	1.287	1.296	121.6	110.1	3.1	8.46	5.26
90	1.384	1.230	1.287	1.294	117.1	110.4	2.5	4.17	1.86
135	1.386	1.233	1.288	1.290	114.6	110.4	3.0	1.55	0.81
trans	1.387	1.235	1.288	1.287	113.3	110.4	3.3	0.00	0.00

[a] Tilt angle of CF_2 groups toward nitrogen lone pair. [b] Total energy $E_t = -582.3146042$ au. [c] $E_t = -583.5542907$ au; both values at the trans configuration.

Table IV. Experimental and Calculated Geometric Parameters (Å, deg) for the Trans Configurations of $H_2C{=}N{-}N{=}CH_2$ and $F_2C{=}N{-}N{=}CF_2$

	$H_2C{=}N{-}N{=}CH_2$			$F_2C{=}N{-}N{=}CF_2$	
	expt[a]	HF	MP2[b]	expt[c]	HF
N—N	1.418 (3)	1.396	1.432	1.421 (12)	1.387
N=C	1.277 (2)	1.253	1.285	1.264 (7)	1.235
NNC	111.4 (2)	112.3	109.8	112.7 (9)	113.3
C—X$_t$	1.094 (5)	1.076	1.076	1.304 (4)	1.288
C—X$_c$		1.080	1.080		1.287
XCX	118.6 (12)	119.2	119.2	110.8 (9)	110.4
tilt[d]	0.0[e]	2.1	2.1	5.0 (8)	3.3

[a] r_a values from ref 13 for −30 °C nozzle temperature. [b] Only the skeletal parameters (N—N, N=C, NNC) were optimized at the MP2 level; the CH_2 parameters correspond to HF level. [c] r_a values from this study. [d] Tilt of CX_2 groups toward nitrogen lone pair. [e] Not refined.

decreases the NNC angle by 2.5° (the values are given in Table IV). For all other dihedral angles the HF values were adjusted accordingly. Since previous calculations for methanimine, $HN{=}CH_2$,[31] had demonstrated that electron correlation has minor effects on the geometry of the CH_2 group, we felt justified to keep these parameters at the HF level. The relative MP2 energies obtained for these "MP2-optimized" geometries (ΔE^{MP}_{MP}) are also included in Table II, and the potential function is displayed in Figure 3 (curve MP2). This potential function is very similar to the MP2 values based on HF geometries. It has a shallow minimum around the 85° dihedral angle, about 0.8 kcal mol^{-1} above the trans configuration. The influence of the geometric parameters (HF- or MP2-optimized) used on the MP2 calculations is small, and we consider the ΔE^{MP}_{MP} values as the best theoretical data available at that time.

Perfluoro-2,3-diaza-1,3-butadiene. Computer-time constraints dictated a rather coarse grid for the dihedral angles in this compound and obviously did not allow geometry optimizations at the MP2 level. The HF-optimized geometries (6-31G* basis set) in steps of 45° and the relative energies (ΔE^{HF}_{HF}) are summarized in Table III, and the torsional potential is displayed in Figure 3. Out of plane distortions for the CF_2 groups are again small and not listed in the table. For the MP2 calculations the geometric parameters for the C=N—N=C skeleton were adjusted by transfering the corresponding differences for the trans conformer of the parent compound (see Table IV) to the HF values of the fluorinated species. This procedure appears to be justified on the basis of previous calculations for $HN{=}CH_2$ and $HN{=}CF_2$, where the effect of electron correlation on the N=C bond length was shown to be nearly independent of fluorination (0.032 and 0.028 Å, respectively).[31] The effect of electron correlation on the C—F bond lengths was transfered from $HN{=}CF_2$.[31] This may not be a perfectly correct estimate of the geometric effects of electron correlation, but the above calculations for $CH_2{=}N{-}N{=}CH_2$ had demonstrated that the internal rotation potential depends only very moderately on the geometry (HF- or MP2-optimized). The ΔE^{MP}_{MP} values (Table III and Figure 3) demonstrate a strong effect of electron correlation on the torsional potential. The coarse grid of points calculated along the internal rotation coordinate and the level of theory (estimated geometries and MP2 approximation), however, do not allow the prediction of quantitative results. The similarity of this potential function with that for $CH_2{=}N{-}N{=}CH_2$ suggests the existence of a second minimum around the 90° dihedral angle and about 1.8 kcal mol^{-1} above the planar trans conformation.

Results and Discussion

The conformational properties of the C=N—N=C skeleton do not change qualitatively with fluorination. In the parent and fluorinated compounds the planar trans structure is predominant and higher energy conformers are observed ($CH_2{=}N{-}N{=}CH_2$) or predicted ($CF_2{=}N{-}N{=}CF_2$). In the perbrominated derivative, however, only the trans-gauche structure with CNNC = 107.9 (5.2)° is observed in an electron diffraction analysis.[32]

The experimental and calculated geometric parameters of 2,3-diaza-1,3-butadiene and the fluorinated species are collected in Table IV. It is well-known that bond lengths at the HF level with 6-31G* basis sets are shorter than experimental values by about 0.02–0.03 Å, and MP2 values are longer by about 0.01–0.02 Å. HF values for bond angles agree with experimental values to within 1–2°.

Fluorination has only minor effects on the skeletal geometries. The calculations predict slight shortening of the N—N bond, but this difference is smaller than the experimental uncertainties. Comparison of the N—N bond lengths in the diaza compounds with those in hydrazines (1.449 (2) Å in $H_2N{-}NH_2$,[33] 1.417 (6) Å in $(CH_3)_2N{-}NH_2$,[34] 1.410 (4) Å in $(CH_3)_2N{-}N(CH_3)_2$[35]) indicates very little or no conjugation in the C=N—N=C skeleton. This is also supported by the ab initio calculations, where (p–p)π overlap populations perpendicular to the molecular plane of 0.008 au in $H_2C{=}N{-}N{=}CH_2$ and −0.020 au in $F_2C{=}N{-}N{=}CF_2$ are predicted. The N=C bonds shorten upon fluorination (0.013 (8) Å from experiment and 0.018 Å from calculations), and this observation is in agreement with an earlier study of the effect of fluorination in methanimine.[31] The NNC angles increase marginally with fluorination. The effective dihedral angle in $CF_2{=}N{-}N{=}CF_2$ (153 (5)°; see Table I) due to the large amplitude torsional vibration around the N—N bond is very similar to the corresponding values for $CH_2{=}N{-}N{=}CH_2$ (160 (5) at 60 °C)[13] and $CH_2{=}C{-}C{=}CH_2$ (157 (2)° at 25 °C).[1]

It is generally assumed[36] that electron correlation has a negligible effect on single-bond rotational potentials, and this has been demonstrated explicitely for 1,3-butadiene[3] and glyoxal.[10a] This, however, is not true for 2,3-diaza-1,3-butadiene, where electron correlation changes the shape of the potential function qualitatively (Figure 3) by introducing an additional minimum and lowers the relative energy at the gauche position by about 3 kcal mol^{-1}. This gauche minimum occurs at a angle slightly larger (~85°) than that obtained from the electron diffraction experiment (62 (20)°), and the energy differences are in good agreement with each other ($\Delta E^{MP}_{MP} = 0.8$, $\Delta E^{expt} = 1.2\ (5)$ kcal mol^{-1}).[13] Electron correlation has a very similar effect on the internal rotation potential of the perfluorinated species, resulting in a shallow gauche minimum about 1.8 kcal mol^{-1} above the trans conformation. This is in reasonable agreement with the experimental estimate of $\Delta G \geq 1.8$ kcal mol^{-1}.

Beside this unexpectedly large effect of electron correlation, the internal rotation potentials in the diaza compounds differ also in other aspects from such potentials in the isoelectronic analogues. Whereas the potential curves of 1,3-butadiene and glyoxal have their maxima around 105 and 75°, respectively, and a low barrier

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(1,3-butadiene) or a minimum (glyoxal) at the cis position, the potential functions for the diaza compounds have their maxima at the cis position. The barriers to internal rotation around the N—N bond are predicted to be much higher (ΔE^{MP}_{MP} = 14.5 and 14.7 kcal mol^{-1}, respectively) than those around C—C bonds (ΔE^{HF}_{HF} = 6.07[3] and 5.7[17] kcal mol^{-1} in 1,3-butadiene and its perfluorinated species or 6.80[10a] and 5.23[20] kcal mol^{-1} in glyoxal or oxalyl fluoride). Further distinct differences between 1,3-butadiene and glyoxal on one hand and 2,3-diaza-1,3-butadiene on the other hand, are the geometry changes occuring during internal rotation. The C—C bond lengths have their minimum values at the trans configuration, their maximum values near the barrier, and intermediate values at the cis position.[3,10c] (The variations of the C—C bond lengths in glyoxal reported in ref 10a differ from those reported in ref 10c.) On the other hand, the N—N bond in CH_2=N—N=CH_2 *shortens* in going from trans to gauche by about 0.028 Å and increases to a maximum value at the cis position. In CF_2=N—N=CF_2 the N—N bond has its maximum length at the trans configuration and shortens monotonically in going to cis. A strong difference between the =C—C= and =N—N= skeletons is also evident from the variations in the bond angles upon internal rotation; whereas the C—C=C and C—C=O bond angles increase only slightly by 3.2 and 1.6° between trans and cis configuration, the N—N=C angles increase by 10.0 and 15.5° in the parent and fluorinated species. This strong angle distortion can be considered as a consequence of the much smaller value for the "unstrained" N—N=C angle in the trans position (112.3°) relative to the corresponding values for C—C=C (124.0°) or C—C=O (121.1°).

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Photophysical, Photochemical, and Electrochemical Properties of Mononuclear and Dinuclear Ruthenium(II) Complexes Containing 2,2′-Bipyridine and the 3,5-Bis(pyridin-2-yl)-1,2,4-triazolate Ion

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The absorption spectra, luminescence spectra (from 77 to 298 K), luminescence lifetimes (from 77 to 298 K), luminescence quantum yields, photochemical quantum yields, and redox potentials of the complexes $Ru(bpy)_2(bpt)^+$ (**1**) and $[Ru(bpy)_2]_2(bpt)^{3+}$ (**2**), where bpy = 2,2′-bipyridine and Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole, are reported. The properties exhibited by **1** and **2** are compared with those of $Ru(bpy)_3^{2+}$. For both **1** and **2**, the lowest energy absorption band and the luminescence band are attributed to Ru → bpy metal-to-ligand charge-transfer (MLCT) singlet and triplet excited states, respectively. Electrochemical oxidation is centered on the metal(s) and electrochemical reduction is centered on the ligands, with bpy being reduced at potentials less negative than those of bpt^-. Because of the stronger σ-donor ability of bpt^- compared with bpy, the Ru → bpy CT absorption and emission bands of **1** (λ_{max}^{abs} = 480 nm and λ_{max}^{em} = 678 nm in CH_3CN at room temperature) are red-shifted compared with those of the parent $Ru(bpy)_3^{2+}$ complex. Both absorption and emission move to higher energies in going from **1** to **2** (for **2**: λ_{max}^{abs} = 453 nm and λ_{max}^{em} = 648 nm). In nitrile rigid matrix at 77 K the emission lifetimes are 2.8 and 3.6 μs for **1** and **2**, respectively. For both complexes increasing temperature causes a strong decrease of the emission lifetime (0.16 μs for **1** and 0.10 μs for **2** at room temperature), but the ln $(1/\tau)$ vs $1/T$ plots between 77 and 298 K are quite different in the two cases, indicating that (i) the luminescent excited state of **1** is much more sensitive than that of **2** to the melting of the solvent matrix and (ii) the luminescent excited state of **2**, but not that of **1**, undergoes a thermally activated (ΔE = 3200 cm^{-1}) radiationless transition to an upper, short-lived excited state (presumably, a triplet metal-centered level ^{3}MC). In agreement with the expectation based on the temperature dependence of the luminescence lifetime, **2**, but not **1**, undergoes a photodissociation reaction in CH_2Cl_2 solutions containing Cl^- ions. Such a photoreaction leads to **1** and $Ru(bpy)_2Cl_2$. All the observed properties show that in **2** the lowest unoccupied molecular orbital does not belong to the bpt^- bridging ligand but to the terminal bpy ligands. Because of the nonequivalence of the coordinating positions of the bridging ligand, in **2** the MLCT and MC levels related to the two $Ru(bpy)_2^{2+}$ units are not isoenergetic. It is found that the lowest excited state of **2** (responsible for the luminescence) is a ^{3}MLCT level centered on one $Ru(bpy)_2^{2+}$ unit, whereas photochemistry takes place from a ^{3}MC level centered on the other $Ru(bpy)_2^{2+}$ unit.

Introduction

Ruthenium(II)–polypyridine complexes constitute a quite large family of coordination compounds. In the past 15 years this family has been the object of extensive investigation related to the interesting photochemical, photophysical, and electrochemical properties of most of its members.[2–6]

In recent years there has been a growing interest toward supramolecular species (dinuclear and polynuclear complexes, host–guest systems, etc.) with the aim to arrive at the design of photochemical molecular devices (proper assemblies of molecular components capable of performing useful light-induced functions).[7] Ruthenium(II)–polypyridine complexes are excellent building blocks for the construction of such devices, especially for light-induced migration and/or collection of electronic energy or electronic charge. Therefore, it is not surprising that the number of investigations concerning the photochemical and photophysical

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