PERKIN 2

The diphosphaallene radical anion: EPR and theoretical investigations

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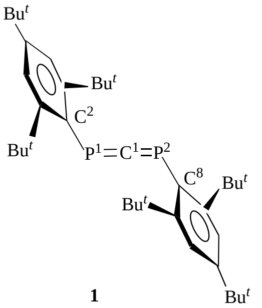
Liquid phase EPR spectra of a diphosphaallenic radical anion have been recorded after electrochemical reduction of a solution of ArP=C=PAr in THF at 293 K (Ar = 2,4,6-$\mathrm{Bu}^t{}_3\mathrm{C}_6\mathrm{H}_2$). The hyperfine coupling interactions of two ^{31}P and one ^{13}C nuclei (in the case of Ar=^{13}C=PAr) are discussed in the light of AM1 calculations carried out on (ArP=C=PAr)$^{\bullet -}$, of *ab initio* calculations performed on the model radical anion (HP=C=PH)$^{\bullet -}$ at the MP2 and MCSCF levels of theory and of DFT calculations on (HP=C=PH)$^{\bullet -}$. The structure of the radical anion is compared with that of the neutral molecule.

Introduction

We have recently shown[1] that diphosphaallene derivatives RP=C=PR can be electrochemically oxidized and that, in the resulting radical cation, the unpaired electron is located in a molecular orbital mainly constituted of a p orbital of each phosphorus atom (*ca.* 20%) and a p orbital of the carbon atom (*ca.* 50%). As shown by *ab initio* calculations[1] on HPCPH—the simplest model compound that retains the allenic character of these species—this oxidation is accompanied by a modification of the molecular geometry. Whereas the HPPH dihedral angle, θ_{HPPH}, is equal to 90° in the neutral molecule, the radical cation has two possible θ_{HPPH} values of *ca.* 45° and *ca.* 135°, corresponding to two isomers of similar energy.

In the present study we show that the diphosphaallene radical anion can be produced by electrolysis of a solution of **1** in THF at low temperature. How reduction affects the electronic structure of diphosphaallenes is the subject of this work.



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Experimental information about the electronic structure of the anion was obtained from the analysis of the hyperfine interactions measured on the EPR spectra of $\mathbf{1}^{\bullet -}$ generated from the ^{13}C-enriched phosphaallene (ArP=^{13}C=PAr). These results are discussed in the light of *ab initio* calculations performed on the model radical anion (HP=C=PH)$^{\bullet -}$. The influence of the cumbersome Ar protecting groups[2] on the conformation of the radical anion is explored by performing semi-empirical calculations on the real species (ArP=C=PAr)$^{\bullet -}$.

Experimental

Generation of the radical anion and EPR experiments

The methods of Yoshifuji *et al.*[3] and of Krieger[4] were used for the synthesis of 1,3-diphosphaallene. The preparation of the ^{13}C-enriched compound has been described in a previous paper.[1] The EPR spectra were obtained on a Bruker E-200 spectrometer (9 GHz, 100 kHz field modulation) equipped with a variable temperature attachment.

The electrochemical reduction of a solution of **1** in THF (10^{-2} M) was carried out inside the EPR cavity by using a platinum electrode and $\mathrm{Bu}^n{}_4\mathrm{NPF}_6$ as an electrolyte. Chemical reduction of **1** was performed by reacting, under vacuum, a thoroughly degassed solution of **1** in THF with a potassium mirror at 258 K. Under reduction (at the surface of the electrode or at the surface of the potassium mirror), the originally colorless solution of **1** turned violet.

Calculations

Ab initio calculations were performed with GAUSSIAN94[5] and HONDO8.5.[6] Semi-empirical calculations were carried out with the AM1 method as implemented in the Gaussian package. This package was also used for DFT calculations.

Results and discussion

EPR spectra

Electrochemical and chemical reductions of **1** lead to EPR spectra exhibiting the same hyperfine structure. Since the spectrum obtained after electrolysis is more intense than that recorded after reaction with potassium, we decided to produce (ArP=^{13}C=PAr)$^{\bullet -}$ only electrochemically. The spectra obtained at 293 K with $\mathbf{1}^{\bullet -}$ and with (ArP=^{13}C=PAr)$^{\bullet -}$ are shown in Fig. 1(*a*) and 1(*b*) respectively. Both spectra are characterized by hyperfine coupling with two equivalent ^{31}P nuclei [$A_{\mathrm{iso}}(^{31}\mathrm{P}) = 215$ MHz], the ^{13}C-enriched anion exhibits an additional coupling with a spin $\frac{1}{2}$ nucleus equal to 27 MHz. As shown in Table 1, these couplings are appreciably different from those obtained for the radical cation[1] or for the monophosphaalkene radical anion.[7]

Decreasing temperature drastically affects the line-width of the signals. Between 315 and 245 K a considerable broadening of the low field and high field signals is observed, below 245 K these lines disappear reversibly. The line-width of the central line progressively increases when temperature is lowered below 288 K. In the 77–164 K temperature range no signal is detectable and it was therefore impossible to measure the anisotropic coupling constants.

Quantum mechanical calculations

The calculations of such species as (2,4,6-$Bu^t_3C_6H_2$)-P=C=P(2,4,6-$Bu^t_3C_6H_2$) is an impossible task for today's quantitative *ab initio* methods. A first view of the structure of this allenic system and its modifications following the addition of one electron was obtained in a preliminary investigation using the AM1 approach (Table 2).

The comparison of the conformation of the neutral system obtained after full geometry optimization, with the molecular structure measured by X-ray diffraction, illustrates the usefulness and limits of the AM1 approach to these cumbersome systems. The calculated P_1–C–P_2 bond angle is only 3° smaller than the experimental angle, while the calculated Ar–P–C bond angle is 6° larger than the experimental one. The central carbon atom C_1 lies in the vicinity of the bisector of the two planes $C_2P_1P_2$ and $C_8P_2P_1$. Both experimental and calculated torsion angles [R–$P_1\cdots P_2$–R] are near to 90°. Moreover, X-ray diffraction as well as AM1 calculations show that each aromatic ring makes an angle of *ca.* 83° with its adjacent CPC plane.

With one electron added in the allenic π system, the molecule does not retain the geometry of the neutral species. As for the positive ion,[1] two conformations are obtained which can be referred to as *cis*-like and *trans*-like with a small energy difference (0.3 kcal mol^{-1}) in favour of the latter structure, Fig. 2.

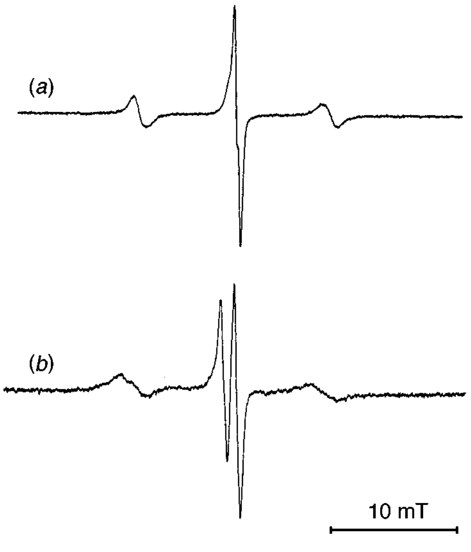


Fig. 1 EPR spectrum obtained at 293 K (*a*) after electrochemical reduction of a solution of ArP=C=PAr in THF, (*b*) after electrochemical reduction of a solution of ArP=^{13}C=PAr in THF

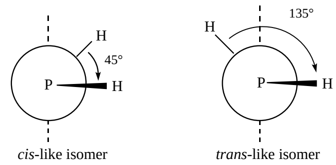


Fig. 2 Rotational isomers of HPCPH

The rotation barrier of the Ar–P bonds around the $P\cdots P$ axis (θ_{RPPR}) decreases from 33 kcal mol^{-1} in the neutral system to *ca.* 5 kcal mol^{-1} in the negative ion. The investigations were not pursued at this level of theory because negative ions require specific considerations of basis sets and correlation effects which cannot be estimated within the AM1 framework.

Looking for a simpler model, we replaced the Ar bulky groups by hydrogen atoms. The validity of the model has been assessed in previous studies[1] on the neutral molecule that showed agreement between the calculated geometrical parameters [for example ∠PCP = 171.9°; ∠HPC = 97.2°; θ_{HPPH} = 90.2° (MC/6-31G**)] and those deduced from the experiment on the larger system (Table 1).

In terms of Lewis localized orbitals of the σ backbone, the electronic configuration of the neutral system is

$$[\mathrm{core}]^{22}\ \sigma_{PH}{}^2\sigma_{PH}{}^2\sigma_{PC}{}^2\sigma_{PC}{}^2 1p_1{}^2 1p_2{}^2\pi_1{}^2\pi_2{}^2 \qquad \text{(a)}$$

where the four highest orbitals, namely, the two lone pairs on the phosphorus atoms and the two π bonds, contain the eight most active electrons of this system, the negative ion being generated by adding one electron to an empty π* orbital.

$$[\mathrm{core}]^{22}\ \sigma_{PH}{}^2\sigma_{PH}{}^2\sigma_{PC}{}^2\sigma_{PC}{}^2 1p_1{}^2 1p_2{}^2\pi_1{}^2\pi_2{}^2\pi^{*1} \qquad \text{(b)}$$

The neutral molecule has been the subject of a few theoretical investigations that predicted an allenic type structure.[8,9] We have recently shown[1] how this system is affected by oxidation using increasing levels of theory, going from MP2 calculations (with no frozen electrons) to multiconfigurational treatments. A similar series of calculations is presented here for the negative ion.

The complete active space of CASSCF calculations, the CAS/basis set, is generated by adding the extra electron to the same orbital space used for the neutral system, distributing nine electrons instead of eight in the two lone pairs on the phosphorus atoms and in the two π and two π* orbitals,

$$[\mathrm{core}]^{30}\ [1p_1 1p_2 \pi_1\pi_2\pi_1{}^*\pi_2{}^*]^9 \qquad \text{(c)}$$

Table 1 EPR parameters of diphosphaallene and phosphaalkene radical ions

Radical ion	$A_{iso}(^{31}P)$/ MHz	$A_{iso}(^{13}C)$/ MHz	*g*
$(ArP{=}^{13}C{=}PAr)^{\bullet -}$	215*	27	2.009
$(ArP{=}^{13}C{=}PAr)^{\bullet +}$ [a]	87*	87	2.0025
$(ArP{=}^{13}C(H)C_6H_5)^{\bullet -}$ [b]	152	16	2.005

[a] Ref. 1. [b] Ref. 7. * Two equivalent nuclei.

Table 2 Conformational parameters for the ArPCPAr diphosphaallene and its negative ion from AM1 calculations and X-ray diffraction experiments

	Conformational parameters/°				
	∠PCP	∠RCP	Torsion angle, $\tau_{C_2PC_1P}$	Dihedral angle, τ_{ArCPC}	Torsion angle, $\theta_{R-P_1\cdots P_2-R}$
ArP=C=PAr					
X-ray	172.5	$C_2P_1C_1$ = 100.3 $C_8P_2C_1$ = 99.9	CP_1CP_2 = 142.1 $C_8P_2C_1P_1$ = 135.9	$ArC_2P_1C_1$ = 80.4 $ArC_8P_2C_1$ = 80.5	83.0
AM1	169.5	$C_2P_1C_1$ = 106.7 $C_8P_2C_1$ = 106.6	$C_2P_1C_1P_2$ = 136.1 $C_8P_2C_1P_1$ = 134.8	$ArC_2P_1C_1$ = 85.1 $ArC_8P_2C_1$ = 85.2	91.7
$ArP{=}C{=}PAr^{\bullet -}$					
AM1 *cis*-like	163.4	$C_2P_1C_1$ = 107.9 $C_8P_2C_1$ = 107.9	$C_2P_1C_1P_2$ = 155.9 $C_8P_2C_1P_1$ = 156.1	$ArC_2P_1C_1$ = 89.2 $ArC_8P_2C_1$ = 89.2	50.7
AM1 *trans*-like	175.0	$C_2P_1C_1$ = 107.4 $C_8P_2C_1$ = 107.4	$C_2P_1C_1P_2$ = 110.1 $C_8P_2C_1P_1$ = 110.1	$ArC_2P_1C_1$ = 77.9 $ArC_8P_2C_1$ = 77.9	141.3

Table 3 Optimized parameters and energies for the $(HP{=}C{=}PH)^{\bullet -}$ radical anion

		Parameters							
Level	Symmetry	r(P–C)/Å	r(P–H)/Å	∠PCP/°	∠HPC/°	τ_{HPCP}/°	θ_{HPPH}/°	Energy (a.u.)	ΔE/kcal mol^{-1}
cis-like isomer									
MP2/6-31 + G**	C_2	1.690	1.423	140.0	99.6	153.3	59.8	−720.7828	0.0
MP2/6-311 + G**	C_2	1.685	1.426	140.0	99.3	152.7	61.0	−721.0901	0.0
CAS/6-31 + G**	C_2	1.708	1.420	146.8	98.7	163.7	35.5	−720.4298	0.0
MC/6-31 + G**	C_2	1.713	1.449	151.5	99.6	162.2	38.2	−720.5193	0.0
B3LYP/6-31 + G**	C_2	1.698	1.449	150.4	99.7	159.3	44.6	−721.9754	0.0
B3LYP/6-311 + G**	C_2	1.693	1.448	148.5	99.6	158.7	46.2	−722.0340	0.0
trans-like isomer									
MP2/6-31 + G**	C_2	1.664	1.434	176.9	101.3	112.8	135.1	−720.7798	1.9
	C_1	1.676	1.425	154.5	100.5	163.8	128.8	−720.7805	1.5
		1.677	1.437		101.3	34.7			
MP2/6-311 + G**	C_2	1.664	1.439	176.1	101.3	113.5	133.8	−721.0863	2.4
	C_1	1.675	1.429	151.8	100.4	161.8	126.7	−721.0877	1.5
		1.673	1.442		101.4	34.5			
CAS/6-31 + G**	C_2	1.692	1.426	177.7	100.2	104.1	152.1	−720.4278	1.3
	C_1	1.700	1.428	156.6	100.4	20.8	148.7	−720.4284	0.9
		1.702	1.422		99.4	167.8			
MC/6-31 + G**	C_2	1.704	1.457	178.8	100.6	104.0	152.2	−720.5187	0.3
	C_1	1.703	1.459	164.1	101.4	21.0	147.1	−720.5186	0.4
		1.711	1.451		100.0	168.2			
B3LYP/6-31 + G**	C_2	1.684	1.458	177.4	101.2	108.7	143.1	−721.9750	0.3
	C_1	1.685	1.457	176.2	101.1	157.2	143.0	−721.9750	0.3
		1.683	1.460		101.3	60.2			
B3LYP/6-311 + G**	C_2	1.680	1.457	177.0	101.1	109.2	142.1	−722.0330	0.6
	C_1	1.684	1.452	168.2	100.5	174.7	141.0	−722.0330	0.6
		1.680	1.461		101.4	34.1			

Table 4 Vibrational analysis of minimum energy structures of neutral (B3LYP/6-311G**) and anionic (B3LYP/6-311 + G**) HPCPH [frequency/cm^{-1} (intensity/km mol^{-1})]

	Neutral B3LYP/6-311G**	*cis*-Like anion B3LYP/6-311 + G**	*trans*-Like anion B3LYP/6-311 + G**	
Symmetry	C_2	C_2	C_2	C_1
asym-PH_{str}	2209 (81)	2067 (269)	1988 (840)	2032 (285)
sym-PH_{str}	2208 (48)	2067 (472)	2010 (44)	1976 (550)
asym-PC_{str}	1330 (57)	1108 (237)	1151 (286)	1142 (282)
asym-HPC_{bend}	829 (58)	798 (7)	773 (9)	778 (14)
sym-HPC_{bend}	821 (28)	823 (11)	802 (10)	798 (11)
$HPCPH_{tors}$	627 (0)	461 (0)	430 (1)	433 (1)
sym-PC_{str}	559 (0)	533 (0)	507 (0)	508 (0)
‖ PCP_{bend}[a]	257 (8)	137 (2)	*i*46 (1)	63 (1)
⊥ PCP_{bend}[b]	261 (11)	328 (24)	295 (10)	300 (11)
ZPE/a.u.	0.02074	0.01896	0.01813	0.01830

[a] Strongly coupled to *sym*-$PC_{stretch}$. [b] Strongly coupled to *sym*-PCH_{bend}.

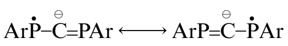
where the core contains the inner shells and the σ_{PH} and the σ_{PC} bonds. As before, a second series of MCSCF calculations, the MC/basis set, was carried out in the full valence space in order to account for the correlation effect of the 17 valence electrons on the σ backbone.

$$[\text{core}]^{22}\,[\sigma_{PH}\sigma_{PH}\sigma_{PC}\sigma_{PC}1p_1 1p_2\,\pi_1\pi_2\pi_1{}^*\pi_2{}^*\sigma_{PH}{}^*\sigma_{PH}{}^*\sigma_{PC}{}^*\sigma_{PC}{}^*]^{17} \quad \text{(d)}$$

In this treatment, the core consists of the inner shells of the carbon and phosphorus atoms. All antibonding orbitals are used in the definition of the active space. The internal level of excitation is limited to doubly excited states with respect to the reference determinant, a level which ensures a correct description of electronic correlation for structural studies.[10] Standard 6-31G** and 6-311G** basis sets were employed, to which diffuse functions were added on the phosphorus and carbon atoms to accommodate the larger expansion of the wave function in the negative ion. The optimized structures are reported in Table 3.

As for the positive ion, the minimum energy structures differ from the neutral parent by an opposite rotation of the P–H bond. The *cis*-like structure of C_2 symmetry is obtained by rotating these bonds so as to reduce θ_{HPPH} from 90° to ≅ 35–60°. The *trans*-like structure of C_2 symmetry is obtained by inverse rotation so as to increase the dihedral angle to ≅ 135–150°. In both systems the P–C bond (1.69 ± 0.02 Å) is longer than in the neutral system (1.66 Å) as a result of the addition of an electron to an antibonding level. The ∠PCP bond angle has closed from ≅ 170° in the neutral molecule to ≅ 145° in the *cis*-like anion due to the repulsion of the electronic charge on the central carbon, but stays almost linear in the *trans*-conformer. The rather large range of variations of the angular parameters (bending or dihedral angles) according to the method used led us to pay more attention to the flexibility of the P–C–P linkage. The results of the vibrational analyses are reported in Table 4 for the neutral molecule and the two conformers of its negative ion.

All *cis*-like C_2 geometries were found to be true minima but *trans*-like C_2 geometries were not. One imaginary frequency was found for the *trans*-like C_2 geometries corresponding to ∠PCP bending (≅ *i*50 cm^{-1}), which suggests that they occupy saddlepoint positions in a shallow potential somewhat displaced from the true minimum. When the C_2 symmetry constraint on the *trans*-like conformation is released, the P–C–P backbone closes by 20–25° in the MP2 and multiconfigurational treatments and becomes close to that of the *cis*-like conformer. The difference between the left and right parts of the molecule is barely significant and the corresponding lowering in energy is less than one kcal mol^{-1}. Using DFT calculations leads to such a shallow potential that the same energy is obtained for the C_1 and C_2 conformers. In any case, these calculations lead us to consider the $HP{=}C{=}PH^{\bullet -}$ anion as a fluxional system with a large flexibility in the P–C–P linkage making description in terms of fixed geometry unrealistic. As shown in Table 4, the main effect to be noticed is the systematic shift of the frequencies towards lower values. This is the direct consequence of the breaking of the π system following the addition of an extra electron to antibonding levels. These results are consistent with the description of the negative ion by the two equivalent allylic structures **2** and **3** (Scheme 1). They rationalize the displacement of the asymmetric P–C–P stretching by $\cong 200$ cm^{-1} towards lower frequencies and the softness of the bending motions. The other vibrations (torsion, bending and stretching P–H) are only slightly affected.



$$\mathrm{Ar\dot{P}{-}\overset{\ominus}{C}{=}PAr \longleftrightarrow ArP{=}\overset{\ominus}{C}{-}\dot{P}Ar}$$

2 **3**

Scheme 1 Valence bond structures for $ArPCPAr^{\bullet -}$

The isotropic coupling constants reported in Table 1 show that the EPR signature of $\mathbf{1}^{\bullet -}$ reflects the probability that the unpaired electron is mainly localized on the two equivalent phosphorus atoms. A difficulty arises from the fact that, in the absence of a frozen solution spectrum, it is impossible to directly know the spin densities in the phosphorus and carbon p orbitals. A comparison between the coupling constants shown in Table 1 with the atomic values[11] indicates that the phosphorus and carbon s spin densities are equal to 0.016 and 0.007 respectively. It is therefore reasonable to infer that such small values are probably due to inner shell polarization and that the unpaired electron is essentially delocalized in the p orbitals of the allenic backbone. Previous single crystal EPR measurements have shown that a spin density of 0.01 in a phosphorus 3p-orbital leads to an $A_{\mathrm{iso}}(^{31}\mathrm{P})$ value of *ca.* 4.2 MHz,[12] while the same spin density in a carbon 2p orbital gives rise to an $A_{\mathrm{iso}}(^{13}\mathrm{C})$ constant equal to *ca.* 1.7 MHz.[13] The $A_{\mathrm{iso}}(^{31}\mathrm{P})$ values given in Table 1 are therefore consistent with a spin density $\rho_{\mathrm{p}} = 0.51$ on each phosphorus atom. The spin density on the central atom is more difficult to evaluate, since the isotropic coupling results from both inner shell polarization and spin polarization through the P–C bonds. In the hypothesis of a negative ^{13}C coupling (−27 MHz) the hyperfine constants of Table 1 would be quite consistent with the allylic structures discussed above.

This interpretation of the EPR spectra can be further substantiated by considering the coupling constants calculated for the *trans*-like and *cis*-like isomers at the MP2 and MCSCF optimized geometries. The values obtained using the MP2 spin density after annihilation of the spin contamination are given in Table 5.

It can be seen that the couplings for the *trans*-like conformation are closer to experiment than the *cis*-like values. This is consistent with the qualitative answer obtained at the semi-empirical level that indicates greater stability for the *trans*-like conformation of the $ArP{=}C{=}PAr^{\bullet -}$ radical. In view of our calculation on the $HP{=}C{=}PH^{\bullet -}$, it appears reasonable to consider C_1 structures rather than C_2, so that the two phosphorus atoms are inequivalent. However, in this hypothesis the C_2 structure is the transition state between two equivalent C_1 structures, represented by the VB structures **2** and **3**. Assuming a fast interconversion motion with respect to the EPR observation time leads to a 50–50% averaging of the phosphorus coupling constants, leaving the carbon coupling unchanged. The values thus obtained, *i.e.* $A_{\mathrm{iso}}(^{13}\mathrm{C}) = -32$ and −36 MHz and $A_{\mathrm{iso}}(^{31}\mathrm{P}) = 214$ and 207 MHz for MP2/6311 + G** and MC/631 + G** respectively, now reproduce the experimental parameters. All the experimental and theoretical information gathered in this study lead us to conclude that reduction of diphosphaallene produces a slightly asymmetric *trans*-like radical anion, which rapidly interconverts between two equivalent structures.

Table 5 ^{31}P and ^{13}C isotropic coupling constants/MHz calculated for the $(HP{=}C{=}PH)^{\bullet -}$ radical anion

	$A_{\mathrm{iso}}(^{31}\mathrm{P})$/MHz	$A_{\mathrm{iso}}(^{13}\mathrm{C})$/MHz
MP2/6311 + G**		
cis-like (C_2)	57, 57	5
trans-like (C_2)	182, 182	−81
trans-like (C_1)	62, 366	−32
MC/631 + G**		
cis-like (C_2)	118, 118	−20
trans-like (C_2)	187, 187	−56
trans-like (C_1)	54, 360	−36

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References

1 M. Chentit, H. Sidorenkova, A. Jouaiti, G. Terron, M. Geoffroy and Y. Ellinger, *J. Chem. Soc., Perkin Trans. 2*, 1997, 921.

2 H. H. Karsch, H.-U. Reisacher and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 618.

3 M. Yoshifuji, K. Toyota and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1984, 689.

4 L. Krieger, Ph.D. Dissertation, University of Bonn, Germany, 1988.

5 GAUSSIAN94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

6 M. Dupuis, F. Johnston and A. Marquez, HONDO 8.5 from CHEM-Station 1994, IBM Corporation, Neighborhood Road, Kingston, NY 12401, USA.

7 M. Geoffroy, A. Jouaiti, G. Terron, M. Cattani-Lorente and Y. Ellinger, *J. Phys. Chem.*, 1992, **96**, 8241.

8 N. J. Fitzpatrick, D. F. Brougham, P. J. Groarke and M. T. Nguyen, *Chem. Ber.*, 1994, **127**, 969.

9 M. T. Nguyen and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1985, 2005.

10 D. Feller, E. S. Huyser, W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1983, **105**, 1459.

11 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.

12 G. Ramakrishnan, A. Jouaiti, M. Geoffroy and G. Bernardinelli, *J. Phys. Chem.*, 1996, **100**, 10 861; M. Geoffroy, E. A. C. Lucken and C. Mazeline, *Mol. Phys.*, 1974, **28**, 839.

13 T. Cole and C. Heller, *J. Chem. Phys.*, 1961, **34**, 1085; H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, 1960, **82**, 766.

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