Diels–Alder reactivity of trialkyl 2-phosphonoacrylates with *N*-buta-1,3-dienylsuccinimide

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***N*-Buta-1,3-dienylsuccinimide 1 reacts quantitatively with trimethyl 2-phosphonoacrylate 2a to furnish the *ortho*-[4 + 2]-cycloadduct 3a as a single stereoisomer. The *cis* axial/equatorial relationship between the succinimido and phosphonate groups respectively has been established by NMR and X-ray diffraction analyses. Triethyl 2-phosphonoacrylate 2b similarly undergoes cycloaddition with the diene 1 to give a 55 : 45 mixture of *ortho* stereoisomers 3b (*cis* axial/equatorial) and 4b (*trans* axial/axial). The activating and directing effect of the phosphonate group is discussed on the basis of a theoretical approach considering the van der Waals complexes.**

Introduction

The synthetic applications of *N*-substituted 1-aminobuta-1,3-dienes in [4 + 2] cycloaddition processes[1] have been well illustrated.[2–10] The usual protection of the terminal dienyl amine involves amide, lactam and carbamate functions;[11–13] such dienes react readily with various olefins bearing an electron-withdrawing group (NO_2, CHO, CO_2R, CN) to furnish exclusively the *ortho*-cycloadducts with a moderate to good *endo*-selectivity.[13–18] On the other hand, the use of *N*-1,3-dienylimides in Diels–Alder reactions is poorly documented.[19]

In connection with studies of biologically active phosphonic derivatives, we required a flexible route towards *ortho*-aminophosphonocyclohexane derivatives which could be further functionalized on the six-membered ring. We selected the Diels–Alder strategy using *N*-butadienylsuccinimide **1**[20] and vinylphosphonates as partners.

Few reports are available on the use of vinylphosphonates as dienophiles.[21–22] They are generally less reactive than the corresponding α,β-unsaturated carbonyl compounds, and the [4 + 2] cycloadducts obtained are mixtures of regio- and stereo-isomers (*endo*/*exo*). Ketovinylphosphonates are more reactive.[23–25] However, the selectivity is directed by the acetyl group; accordingly, the final cycloadducts exhibit the phosphonate group in the *meta* position regarding the activating substituent (OR) placed on the C(1) carbon atom of the diene.

We found that trialkyl 2-phosphonoacrylates **2** react rapidly and quantitatively with *N*-butadienylsuccinimide **1** to furnish *ortho*-cycloadducts as single or major stereoisomers **3**, with a *cis* axial/equatorial relationship between the succinimido and phosphonate groups.

Results and discussion

We first confirmed the poor reactivity of vinylphosphonates as dienophiles: no cycloadduct could be detected (^{1}H NMR and TLC analyses) after refluxing *N*-butadienylsuccinimide **1** and diethyl vinylphosphonate in acetonitrile for two weeks.

Interestingly, we observed a dramatic enhancement of the alkene reactivity by the introduction of a carboxylate substituent in the geminal position. Thus, trimethyl 2-phosphonoacrylate **2a** quantitatively reacted with **1** in acetonitrile at 65 °C. After 48 h, the crude mixture was purified by flash chromatography on silica gel to furnish 3-succinimido-4-dimethylphosphono-4-methoxycarbonylcyclohex-1-ene **3a** as a pale-yellow oil that smoothly crystallized by slow evaporation from a toluene solution (Scheme 1).

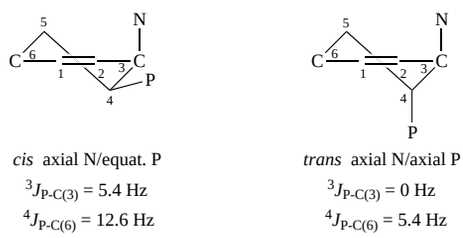
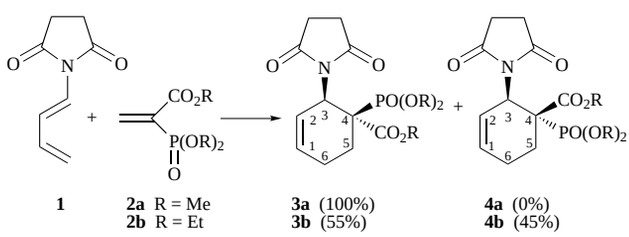


Fig. 1 Characteristic heteronuclear C–P coupling constants



1 **2a** R = Me, **2b** R = Et; **3a** (100%), **3b** (55%); **4a** (0%), **4b** (45%)

Scheme 1 Cycloaddition of trialkyl 2-phosphonoacrylates

The ^{1}H and ^{13}C NMR spectra of **3a** confirmed the presence of a single regio- and stereo-isomer; they involve characteristic features related to the half-chair conformation adopted by the compound, and to the *cis* axial/equatorial relationship between the succinimido and phosphonate groups respectively, as further revealed by the X-ray diffraction analysis. The high value (*J* 18.7)† for the coupling constant between the two geminal protons H(6) is relevant. The carbon atoms of the imidyl carbonyls gave two broad signals (176.6 and 177.3 ppm), strongly suggesting that the rotation of the succinimido group around the N–C(3) bond is hindered by the *cis* bulky phosphonate group. Two heteronuclear C–P coupling constants appeared to be particularly influenced by the axial/equatorial position of the phosphorus atom (Fig. 1): the $J_{P\text{–}C(3)}$ and $J_{P\text{–}C(6)}$ values were 5.4 and 12.6 respectively for compound **3a** having the phosphonate group in the equatorial position.

Triethyl 2-phosphonoacrylate **2b**[26] was similarly reacted with the diene **1** (Scheme 1): after 4 d at 65 °C in acetonitrile,

† *J* values in Hz.

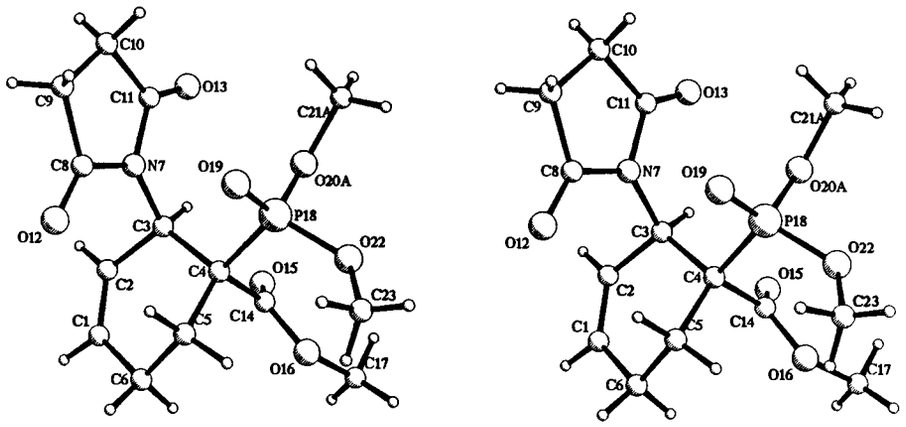


Fig. 2 Stereoscopic view of **3a** (PLUTO)[27]

Table 1 Endocyclic torsion angles in the cyclohexene ring of **3a**

	Angle (°)
C(6)–C(1)–C(2)–C(3)	3.7(4)
C(1)–C(2)–C(3)–C(4)	8.4(3)
C(2)–C(3)–C(4)–C(5)	−38.5(2)
C(3)–C(4)–C(5)–C(6)	57.9(2)
C(2)–C(1)–C(6)–C(5)	15.6(4)
C(4)–C(5)–C(6)–C(1)	−45.5(3)

I (*gauche* configuration) II (staggered configuration)

X = CO_2H 0.0 kcal mol^{-1} 7.80 kcal mol^{-1}

X = CN 0.0 kcal mol^{-1} 4.92 kcal mol^{-1}

Fig. 3 Isomerization energies of model cyclohexenes

a mixture of two *ortho*-adducts **3b** and **4b** was quantitatively recovered. According to the ^{1}H and ^{13}C NMR data, the ratio of stereoisomers was 55:45, in favour of **3b**. This major compound showed the same spectral characteristics as the reference compound **3a** ($J_{P–C(3)}$ 5.4 and $J_{P–C(6)}$ 12.6); we deduced a *cis* axial/equatorial relationship between the succinimido and phosphonate groups. We could reasonably attribute the *trans* axial/axial stereochemistry to the minor isomer **4b**. For this isomer, free rotation of the succinimido group around the N–C(3) bond could occur; accordingly, one sharp line was observed at 176.3 ppm for the two equivalent imidyl carbonyls. The axial position of the phosphorus atom significantly influenced the relevant heteronuclear C–P coupling constants: the P–C(3) coupling was suppressed and the P–C(6) coupling appeared considerably diminished (*J* 5.4) (Fig. 1).

The configuration of the cycloadduct **3a** was unambiguously confirmed by a single crystal X-ray diffraction analysis. As shown in the stereoscopic view of the molecule (Fig. 2),[27] the succinimido and the phosphonate groups are *cis* to each other, respectively in *pseudoaxial* and *pseudoequatorial* positions. Selected geometrical parameters are presented in Table 1 and are available as supplementary material. We have calculated average values of P=O, P–O and P–C bond lengths over 62 structures of acyclic phosphonate derivatives bonded to a C sp^3 atom;[28] they are respectively 1.460, 1.563 and 1.815 Å. The observed values in **3a** [1.445(2), 1.560(2) and 1.832(2) Å] compare quite well with these means. As shown by the endocyclic torsion angles (Table 1), the cyclohexene ring adopts a half-chair conformation with the diad axis through the midpoint of the double bond [$\Delta C_2(1–2) = 7.1°$].[29]

In relation with the observed selectivity (*endo* directing effect of the phosphonate group), it is worth noting the orientation of the succinimido towards the phosphonate group. The best mean planes through the succinimido ring and through O=P–O20 (A or B) are nearly parallel to each other, the dihedral angle between the two planes being *ca*. 8°. 8.6° for orientation A of O20 and 8.4° for orientation B of O20. We have found in the literature only one phosphonate derivative with a similar substituent in the γ-position with respect to the P atom: (*E*)-diisopropyl 1-hydroxyimino-2-phthalimido-3-phenylpropylphosphonate.[30] In this molecule, the planes of the phthalimido and O=P–O are also parallel with the same dihedral angle of 8° as that observed in **3a.**

The Diels–Alder cycloadditions involving 1,1-disubstituted partners can proceed either by a concerted process or not.[31–34] Whatever the mechanism involved, the selectivity leading to the relative *cis*-configuration of the imido and phosphonate groups in the final cyclic products **3** could be inspected theoretically.

From a theoretical point of view, a first approach would consist of a comparison of the isomers related to the products in order to determine their relative stability (the most stable compound being the expected product). To facilitate such theoretical approaches *ab initio*, one must define a model for the adduct molecules. To this end, methyl (or ethyl) groups were replaced by hydrogen atoms correctly orientated to avoid hydrogen bonding between substituents which would artificially stabilize such structures. Further, the methylene groups of succinimide were also replaced by hydrogen atoms. This model leads to two isomers (I and II) depending on the relative positions of the imido and phosphonic groups. Fig. 3 reports the relative energies provided by the *ab initio* calculations at the RHF/6-31G(d,p) level. These results show that in spite of the steric effect resulting from the closeness of two bulky substituents, the *gauche* configuration is preferred to the staggered one. To confirm this result and verify the independence of the effect on the nature of the carboxylic substituent, the latter has been replaced by a cyano group. Even though the stabilization is less effective, the sterically favoured staggered configuration is less stable.

This unexpected result suggests that some particular interactions may exist between the imido and phosphonic groups. In this hypothesis, the reactivity would be governed by such interactions which must be present all along the reaction path, especially in the van der Waals pre-reactive complexes. In this preliminary approach, we have searched for such complexes between the substituted *cis* butadiene and ethylene moieties and localized two of these on the energy hypersurface. The stabilization of the complexes *versus* the reactant molecules ranges from 7.9 to 10.1 kcal mol^{-1} (1 cal = 4.184 J) for the CO_2H substituent, and from 4.2 to 5.9 kcal mol^{-1} for the CN substituent. For comparison, such a complex between *cis*-butadiene and ethylene is stabilized by 1.7 kcal mol^{-1}. The two complexes found

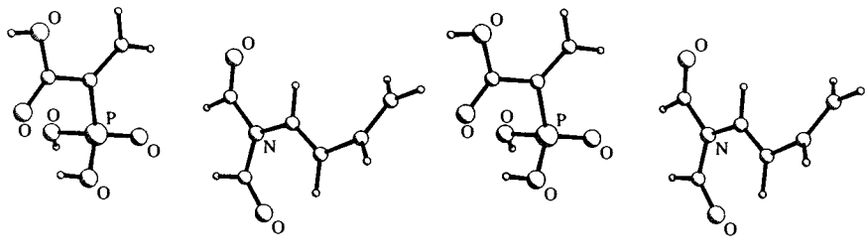


Fig. 4 Phosphonoacrylate van der Waals complex

present a strong interaction between the imido part and the phosphonic group, the cyano or the carboxylic group. A stereo-view of one of those complexes is shown in Fig. 4. In the absence of hydrogen bonding, the most stable complexes are obtained with the phosphonic group coming close to the imido part. It is our opinion that the strength of the complexes keeps the two reaction sites together long enough for a selective reaction to take place.

Even though preliminary, these results lead to the conclusion that favourable van der Waals interactions appear to occur between the phosphonate and succinimido substituents, which might govern the further reactivity of these species and produce a Diels–Alder adduct despite the steric hindrance.

Conclusions

The remarkable reactivity of phosphonoacrylates in [4 + 2] cycloaddition with butadienylsuccinimide opens a route towards functionalized cyclohexane derivatives equipped with vicinal amino and phosphono groups (*ortho* products).

We have pointed out that the geminal substitution of the alkenes strongly enhances their dienophilic reactivity, as compared to the corresponding monosubstituted derivatives. In a control experiment, we have reacted butadienylsuccinimide **1** with methyl acrylate; after 6 d at 65 °C in acetonitrile, the rate of conversion into Diels–Alder product was *ca*. 80%. Under similar conditions, vinylphosphonates were totally unreactive, while the transformation of phosphonoacrylates was complete within 2–4 d.

From a stereochemical point of view, we have revealed an unexpected selectivity in favour of the *cis* axial/equatorial cycloadducts **3**; in terms of Alder's rule, the phosphonate substituent exercises a more potent *endo* directing effect than the carboxylate substituent. This observation constitutes the first report of such a selectivity when PO_3R and CO_2R groups are in direct competition facing a 1-substituted butadiene.

We could tentatively explain our results by the presence of an imido *N*-protective group. This particular moiety creates favourable interactions with the phosphonate substituent, as found experimentally in the X-ray structure [CONCO/P(O)O stacking], and confirmed theoretically: the most constrained *cis* isomer **3** (R = H) was significantly stabilized regarding the less sterically hindered *trans* isomer **4** (R = H; relative energy: 7.8 kcal mol^{-1}). Accordingly, particular interactions were found in the pre-reactive complex leading to the *cis* stereoisomer **3** (R = H).

The theoretical predictions applied perfectly to the cycloaddition of trimethyl 2-phosphonoacrylate (R = Me). However, using the more bulky triethyl 2-phosphonoacrylate (R = Et), a mixture of cycloadducts **3** (*cis*, N axial/P equatorial) and **4** (*trans*, N axial/P axial) was recovered, most probably resulting from the competition between favourable stacking interactions and unfavourable steric interactions due to the P–O–R chains.

Experimental

General

Reagents and solvents were purchased from Aldrich. The IR spectra were taken with a Perkin-Elmer 1710 instrument and calibrated with polystyrene. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer, in $CDCl_3$ solution; chemical shifts are reported in ppm (δ) downfield from internal Me_4Si (J in Hz). The mass spectra (FAB or EI modes) were obtained on a Finnigan MAT TSQ-70 instrument. The microanalyses were performed at University College London by Dr Alan Stones.

N-Buta-1,3-dienylsuccinimide **1** was obtained by refluxing succinimide and crotonaldehyde in toluene in the presence of toluene-*p*-sulfonic acid as catalyst, followed by flash chromatography on silica gel (230-400 mesh ASTM, supplied by Merck) with ethyl acetate–hexane (25 : 75) as eluent.[13] Trimethyl 2-phosphonoacrylate **2a** was commercially available (Aldrich). Triethyl 2-phosphonoacrylate **2b** was obtained from triethyl-phosphonoacetate by reaction with paraformaldehyde and piperidine in refluxing methanol, followed by distillation over phosphoric acid.[26]

3-Succinimido-4-dimethylphosphono-4-methoxycarbonyl-cyclohex-1-ene 3a

N-Buta-1-3-dienylsuccinimide **1** (300 mg, 1.98 mmol), trimethyl 2-phosphonoacrylate **2a** (308 mg, 1.58 mmol) and hydroquinone (60 mg, 0.54 mmol) were dissolved in acetonitrile (2 ml) and heated under an argon atmosphere at 65 °C for 48 h. After solvent evaporation, the crude mixture was purified by flash chromatography on silica gel (230–400 mesh ASTM, supplied by Merck) with dichloromethane–isopropyl alcohol (1 : 1) as eluent. Yield: 638 mg (93%); mp 99–101 °C (from toluene); ν_{max}/cm^{-1} (CH_2Cl_2) 3458 (m), 2959 (w), 1709 (s), 1600 (w), 1434 (w), 1389 (w), 1358 (m), 1250 (m), 1177 (m), 1030 (m); δ_H(500 MHz) 2.19 (m, H-6), 2.30 (dt, H-6′, $J_{(6,6')}$ 18.7), 2.39 (dt, H-5, $J_{(5,5')}$ 13.6), 2.71 (m, H-5′), 1.71 (br s, CH_2 imide), 3.70 (d, OCH_3 phosphonate, $J_{H\text{-}P}$ 11.0); 3.79 (d, OCH_3 phosphonate, $J_{H\text{-}P}$ 11.0) 3.79 (s, OCH_3 ester), 5.43 (m, H-2), 5.65 (m, H-3), 6.02 (m, H-1); δ_C(125 Hz) 21.47 (d, C-6, $J_{C\text{-}P}$ 12.6), 21.88 (C-5), 27.80 (CH_2 imide), 45.58 (d, C-3, $J_{C\text{-}P}$ 5.4), 52.35 (d, C-4, $J_{C\text{-}P}$ 135.0), 52.93 (OCH_3 ester), 53.19 (d, OCH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 54.18 (d, OCH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 120.45 (d, C-2, $J_{C\text{-}P}$ 90), 131.48 (C-1); 169.12 (d, CO ester, $J_{C\text{-}P}$ 5.4), 176.62 (br s, CO imide), 177.34 (br s, CO imide); MS *m/z* (FAB) 346 (M + 1) (Found: C, 48.66; H, 5.80; N, 3.59. Calc. for $C_{14}H_{20}NO_7P$: C, 48.69; H, 5.83; N, 4.05%).

3-Succinimido-4-diethylphosphono-4-ethoxycarbonylcyclohex-1-ene 3b and 4b. The succinimide **1** (125 mg, 0.826 mmol), **2b** (190 mg, 0.804 mmol) and hydroquinone (14.2 mg, 0.128 mmol) were heated in acetonitrile (1 ml) at 65 °C for 4 d (under Ar), as above. Yield: 312 mg (98%, yellow oil); ν_{max}/cm^{-1} (CH_2Cl_2) 3475 (m), 2982 (w), 1711 (s), 1636 (w), 1445 (w), 1389 (w), 1357 (m), 1248 (m), 1177 (m), 1023 (m); *cis* isomer **3b** (major): δ_H(500 MHz) 1.17–1.36 (t, 9H, CH_3 ester + CH_3 phosphonate), 2.14–2.35 (m, H-6 + H-6′), 2.39 (dt, H-5, $J_{(5,5')}$ 13.7), 2.68 (m, H-5′ + br s, CH_2 imide), 3.94–4.27 (q, 6H, OCH_2 ester + OCH_2 phosphonate), 5.44 (m, H-2), 5.69 (m, H-3), 6.02 (m, H-1); δ_C(125 MHz) 13.77 (CH_3 ester), 16.00 (d, CH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 16.30 (d, CH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 21.65 (d, C-6, $J_{C\text{-}P}$ 12.6), 21.90 (C-5); 27.96 (CH_2 imide), 45.76 (d, C-3, $J_{C\text{-}P}$ 5.4), 52.56 (d, C-4, $J_{C\text{-}P}$ 132.8), 61.79 (OCH_2 ester), 62.78 (d, OCH_2 phosphonate, $J_{C\text{-}P}$

7.2), 63.56 (d, OCH_2 phosphonate, $J_{C\text{-}P}$ 7.2), 120.76 (d, C-2, $J_{C\text{-}P}$ 9), 131.57 (C-1), 168.74 (d, CO ester, $J_{C\text{-}P}$ 5.4), 176.56 (br s, CO imide), 177.43 (br s, CO imide); *trans* isomer **4b** (minor): δ_H(500 MHz) 1.17–1.36 (t, 9H, CH_3 ester + CH_3 phosphonate), 2.14–2.35 (m, H-6 + H-6′), 2.56 (m, H-5 + H-5′), 2.68 (br s, CH_2 imide), 3.94–4.27 (q, 6H, OCH_2 ester + OCH_2 phosphonate), 5.30–5.40 (m, H-2 + H-3), 6.02 (m, H-1); δ_C(125 MHz) 13.64 (CH_3 ester), 16.13 (d, CH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 16.23 (d, CH_3 phosphonate, $J_{C\text{-}P}$ 7.2), 22.15 (d, C-6, $J_{C\text{-}P}$ 5.4), 24.14 (d, C-5, $J_{C\text{-}P}$ 3.6), 27.86 (CH_2 imide), 46.40 (C-3), 50.23 (d, C-4, $J_{C\text{-}P}$ 131.1), 61.48 (OCH_2 ester), 62.66 (d, OCH_2 phosphonate, $J_{C\text{-}P}$ 7.2), 63.33 (d, OCH_2 phosphonate, $J_{C\text{-}P}$ 7.2), 121.62 (d, C-2, $J_{C\text{-}P}$ 5.4), 130.58 (C-1), 168.84 (d, CO ester, $J_{C\text{-}P}$ 5.4) 176.27 (CO imide). MS *m/z*(EI) 387 (M) (Found: C, 52.69; H, 6.88; N, 3.35. Calc. for $C_{17}H_{26}NO_7P$: C, 52.71; H, 6.76; N, 3.61%).

X-Ray analysis and structure determination

Crystallographic data for **3a**: $C_{14}H_{20}NO_7P$, $M_r = 345.28$, triclinic, $P\bar{1}$, $a = 8.688(2)$, $b = 8.907(1)$, $c = 12.424(1)$ Å, $\alpha = 88.71(2)$, $\beta = 75.73(2)$, $\gamma = 61.97(2)°$, $V = 817.6(2)$ Å^3, $Z = 2$, $D_c = 1.403$ g cm^{-3}. Parallelipiped crystal with approximate dimensions 0.4 × 0.3 × 0.3 mm. Lattice parameters were refined using 30 reflections in the range $5 \leqslant 2\theta \leqslant 25°$. Huber four-circle diffractometer, graphite monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å). 3210 independent reflections with $\sin\theta/\lambda \leqslant 0.62$ Å^{-1}; $0 \leqslant h \leqslant 10$, $-9 \leqslant k \leqslant 10$, $-14 \leqslant l \leqslant 15$, 2471 with $I \geqslant 2(I)$. A standard reflection (0 −2 −1) was checked every 50 reflections; no significant deviation was observed. The structure was solved by direct methods using SHELXS86.[35] All H atoms, except those of one methyl group, were located from difference Fourier synthesis; the H atoms of methyl C21 were calculated with AFIX. Anisotropic least squares refinement (SHELXL93)[36] using F^2 values; H isotropic with a common refined thermal parameter ($U = 0.079$ Å^2). 279 parameters. $w = 1/\sigma^2(Fo)^2 + 0.078P^2 + 0.03P$). Two positions appeared for the methoxy group O20–C21; the occupation factors of the two positions converge to 0.78 (A) and 0.22 (B) at the end of the refinement. Final R indices; $R = 0.046$, R (all data) = 0.059, $wR2 = 0.12$, $S = 1.07$. Final maximum shift to error = 0.001. Maximum and minimum heights in final Fourier synthesis = 0.44 and −0.30 e Å^{-3}. Atomic scattering factors from ref. 37.†

Theoretical analysis

The molecules and van der Waals complexes under investigation have been studied at the restricted Hartree-Fock (RHF) level using the 6-31G(d,p) basis set of Hariharan and Pople.[38] Such a basis gives enough flexibility to the wavefunction to ensure a balanced behaviour of the phosphorus atom. The geometric structures obtained in this paper result from a full geometry optimization of all the considered parameters in the $3N - 6$ internal coordinates space, thus relaxing any *a priori* symmetry constraint. A conventional gradient technique was used for the search of the optimal structure. The analytical computation of the first and second derivatives of the energy hypersurface guarantees the good behaviour of the extremum found. All the computations reported in this paper were obtained using the GAUSSIAN series of programs.[39] Due to the presence of labile intermolecular parameters, the potential energy surface of the complexes is very flat. This leads to some looseness of the obtained structures which, nevertheless, have the properties of a true minimum.

† Atomic co-ordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/89.

Acknowledgements

This work was generously supported by the Fonds National de la Recherche Scientifique (FNRS, Belgium), the Fonds du Développement Scientifique (FDS, UCL, Belgium), and the Institut de Recherches Servier (Suresnes, France). N.D. and J.M.-B. thank Dr A. Cordi for stimulating discussions.

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Paper 7/02324C
Received 4*th April* 1997
Accepted 23*rd June* 1997