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Conformer determination of stabilized triphenyl phosphonium acyl ylides by infrared spectroscopy

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ABSTRACT

Stretching frequencies of acyl groups of stabilized triphenyl phosphonium ylides with ester, keto or cyano groups depend in part on the orientations of the acyl groups, *syn* or *anti*, with respect to phosphorus. Frequencies predicted by *ab initio* HF methods are higher than observed, and for diesters and diketones are higher for *anti* than *syn* acyl groups. For diester and diketo ylides and their cyano derivatives a Scale Factor, SF, of 0.866, fits much of the data with HF/6-31G(d) calculations, although it is lower than the literature value. The literature SF values for DFT methods, e.g., BLYP/6-31G(d) and B3LYP/6-31G(d), are closer to unity, and agreement with experiment is reasonable, except that for mixed *anti* isopropyloxy or *t*-butyloxy and *syn* methoxy or ethoxy diester ylides predicted stretching frequencies of the *syn* acyl groups by BLYP are too low, and fits are worse than with HF/6-31G(d), but B3LYP gives satisfactory results. The combination of *ab initio* methods and determination of IR acyl stretching frequencies may be useful when structure determination of stabilized ester, keto and cyano ylides by X-ray crystallography is not feasible, or when conformer interconversion in solution is too fast for use of NMR spectroscopy.

1. Introduction

Phosphonium ylides with one keto or ester group can take up conformations with the acyl oxygen oriented towards, or away from, phosphorus, designated *syn* or *anti*, respectively, and classical structures can be written with a P—C single bond and a double bond between the ylidic and acyl carbons [1–3]. There is a significant energy difference between the conformers because of the favorable interaction between a *syn* anionoid acyl oxygen and cationoid phosphorus (Scheme 1). There is also a significant energy barrier to interconversion of the conformers because of loss of resonance energy with rotation about the bond between the ylidic and acyl carbons, and in favorable cases individual conformers can be identified by NMR spectroscopy [2,4,5].

The situation is more complicated when there are two acyl groups, as in stabilized phosphonium ylides, because rotation about one of the bonds between the ylidic and acyl carbons does not preclude the resonance interaction involving the other acyl group, see Scheme 2 [6–10]. As a result estimated energy barriers for interconversion of conformers are much lower than those for monoacyl derivatives, and conformers do not have very different energies. We define conformations of stabilized diester or diketo ylides as *syn* or *anti* in terms of orientations of the two acyl groups with respect to phosphorus.

Classical structures shown in Schemes 1 and 2 are inadequate in that the bonds between the ylidic carbon and phosphorus, or to the acyl carbons, are intermediate in length between single and double bonds and there is free rotation about the C—P bond on the NMR time scale. A classical structure can reasonably be written as zwitterionic [11], with a C—P single bond, and electronic delocalization between the ylidic and acyl groups.

The substituents on phosphorus can be alkyl or aryl, but all the phosphonium ylides discussed here are triphenyl derivatives. Typically one conformer is dominant in the crystal [12–15], although later we note an exception to this generalization. There is a balance between covalent and noncovalent interactions, and, provided that suitable crystals can be isolated, conformations can be determined by X-ray crystallography. At the simplest level, by analogy with the behavior of monoacyl ylides [1–3], *syn–syn* conformers should be preferred, and *ab initio* computations for isolated (gas phase) molecules support this assumption [6,7]. However, so far as we know, *syn–syn* conformers of diesters have not been observed, probably because, as discussed later, intra- and intermolecular noncovalent interactions disfavor them [6–10]. For example, interference between bulky alkoxy groups, *anti* to phosphorus, should be destabilizing. In going from a *syn*- to an *anti*-orientation of an ester group interaction of an acyl oxygen with phosphorus is partially offset by interaction with the alkoxy group, consistent with estimation of

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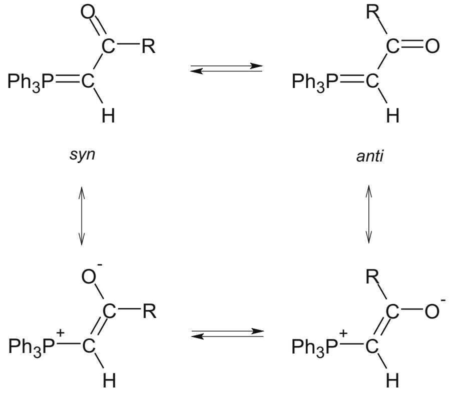
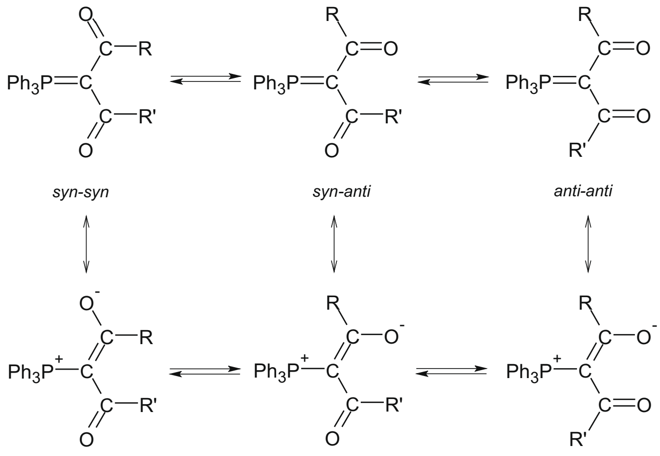


Scheme 1. Conformations of phosphonium ylides with one keto or ester group. R = alkyl, alkoxy.

Partial Atomic Charges [10,16]. The situation is different if one ester or keto group is replaced by a linear cyano group, which does not interfere with its neighbor, and the acyl oxygen is then preferentially *syn* to phosphorus [17,18].

Examination of ^{1}H, ^{13}C, and ^{31}P NMR spectra provides useful structural information but, unlike the situation for monoacyl derivatives, rotations about the ylidic bonds may be fast on the NMR time scale and information will then be for time-averaged conformers [19]. In favorable cases, where one conformer is dominant, evidence for orientation towards phosphorus of an alkoxy group in an ylidic ester is provided by observation of π-shielding in the signal of a terminal **CH**$_3$ group oriented towards the face of a phenyl group [7,10,12]. The time-scale limitations of NMR spectroscopy do not apply to Infrared, IR, and Raman spectroscopy [19], and the former is very useful in identifying functional, especially polar, groups. For example, strong IR signals of carbonyl and cyano groups are readily identified in stabilized ylides, are usually well separated from other signals [20], and we limit our observations to these signals which should be sensitive to conformation. Accurate frequency measurement is not essential when IR spectroscopy is used only for identification of functional groups, or information from signals in the "fingerprint" region. Infrared spectroscopy lacks the quantitative power of NMR spectroscopy, but, in favorable cases, comparison of observed and predicted stretching frequencies of acyl or cyano groups should provide information on the environment of that group in the ylidic system. Frequencies can be predicted at various computational levels, but Hartree Fock (HF) methods give frequencies that are consistently too high, because of systematic errors in estimating force constants [16], and Scott and Radom [21], in a very extensive study of many organic and inorganic compounds, showed that errors in the HF/6-31G(d) method are reasonably constant, and can be corrected with a Scale Factor, SF, of 0.8953 [21]. These results show that this simple treatment should be generally useful, and similar SF values apply to other HF treatments. The Density Functional Theory (DFT) and Moller–Plesset (MP2) treatments have SF values significantly closer to unity, but overall results are not necessarily better than from the simpler HF treatment [16,21]. The BLYP/6-31G(d) method has an SF value of 0.9945 [21], which can generally be neglected within the usual errors of frequency measurement, and is an attractive feature of this method, but for the hybrid functional B3LYP/6-31G(d), with SF = 0.9614, the correction cannot be neglected [16,21]. There are inevitable questions regarding appropriate SF values for particular classes of compounds [22]. Because of the simplicity of the HF/6-31G(d) method and independent evidence for the near unity SF value of the DFT functional BLYP/6-31G(d) we generally used these treatments.



Scheme 2. Conformations of stabilized acyl ylides. R and R′ = alkyl, alkoxy.

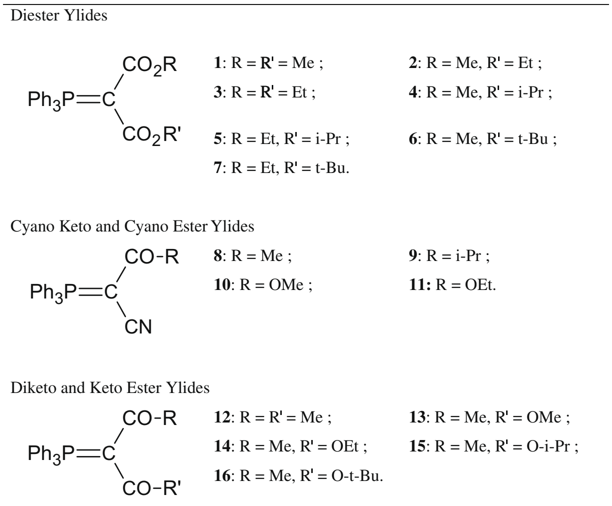
We examined *ab initio* frequency predictions with stabilized triphenyl phosphonium ylides with known, or readily inferred, conformations, and structures are in Chart 1. Geometries and frequency predictions were initially from HF/6-31G(d) optimizations, but BLYP/6-31G(d) and B3LYP/6-31G(d) were also used and the ester groups always adopted the *Z* orientation, as for free carboxylic esters [23]. Conformations of most of these ylides are from X-ray crystallography [9,13–15,18], but those of **9** and **11** are inferred from examination of ^{1}H NMR spectroscopy and by analogies with structures of similar ylides (Chart 1). The symbols s and a are used in the Text and Tables to indicate *syn* and *anti* acyl groups, respectively.

Infrared spectra of these stabilized ylides are complex and although some vibrations, e.g., of the PC bond in the phosphonium moiety can be identified at approximately 530 cm^{-1}, there is often signal overlap and strong coupling with other motions. However, signals of acyl and cyano stretching vibrations are generally separated from other signals and we used them in our comparisons of predicted and observed frequencies.

2. Experimental

2.1. Materials

Most ylides have known conformations and had been prepared by transylidation reactions of mono ester, ketone or cyano ylides



Most of these compounds have conformations from X-ray [9,13-15,18] except for **9** and **11**.

Chart 1. General structures of stabilized acyl ylides.