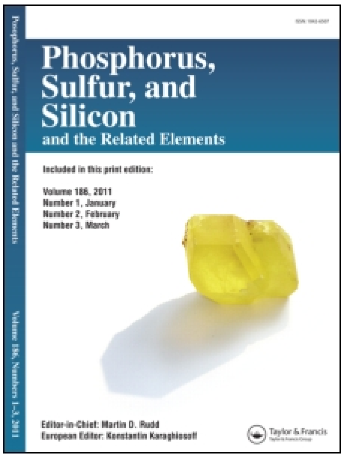

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Aitken, R. Alan , Kozminykh, Elena N. , Kozminykh, Vladislav O. and Lightfoot, Philip(1998) 'Solution and Solid State Structure of Highly Delocalised 5- Triphenylphosphoranylidenecyclopen Tene-3,4-Diones', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 487 — 492

To link to this Article: DOI: 10.1080/10426509808545489

URL: http://dx.doi.org/10.1080/10426509808545489

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 487–492
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SOLUTION AND SOLID STATE STRUCTURE OF HIGHLY DELOCALISED 5-TRIPHENYLPHOSPHORANYLIDENECYCLOPENTENE-3,4-DIONES

R. ALAN AITKEN[a]*, ELENA N. KOZMINYKH[b], VLADISLAV O. KOZMINYKH[b] and PHILIP LIGHTFOOT[a]

[a] *School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom and* [b] *Laboratory for the Synthesis of Biologically Active Compounds, Perm Pharmaceutical Academy, P.O. Box 8519, Perm-51, 614051, Russia*

(Received 16 April, 1998)

The fully assigned ^{13}C NMR spectra of the cyclic ylides 4 and 5 show that the C-1-C-2 bond is very strongly polarised consistent with substantial delocalisation of the ylide negative charge on to C-2. The X-ray structure of 5 confirms the occurrence of extensive delocalisation involving a significant contribution from up to six separate resonance forms.

Keywords: Phosphorus ylides; X-ray structure; ^{13}C NMR spectra; delocalisation; cyclic ylides

Some time ago, some of us reported the reaction of ethyl triphenylphosphoranylidenepyruvate **1** with 5-aryl-2,3-dihydrofuran-2,3-diones **2** and **3** to give products which were assigned the unusual structures **4** and **5** on the basis of elemental analysis, IR and ^1H NMR spectra.[1] We now present fully assigned ^{13}C NMR spectra for **4** and **5** and the result of a single crystal X-ray diffraction study on **5** which not only confirm the proposed structures but clearly show that there is extensive delocalisation involving up to six resonance forms.

The ylides **4** and **5** were prepared as described previously,[1] and the good quality ^{13}C NMR spectra obtained in $CDCl_3$ are presented in Table I. In order to assign these fully we made use of the highly informative pattern of P-C coupling which extends throughout the P-phenyl groups and the cyclopentene ring and to the ester carbonyl. The resulting coupling constants are not only consistent between **4** and **5**, but also in agreement with the values previously reported for

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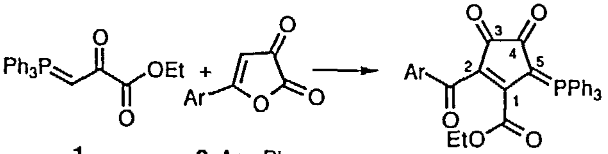
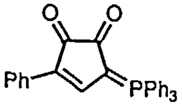
* Corresponding author.



1

2 Ar = Ph
3 Ar = 4-MeC$_6$H$_4$

4 Ar = Ph
5 Ar = 4-MeC$_6$H$_4$



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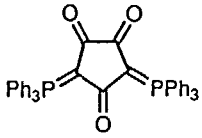

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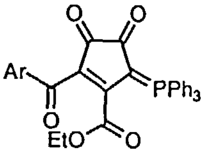

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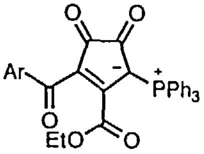

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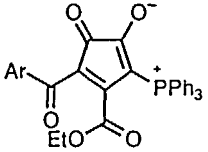

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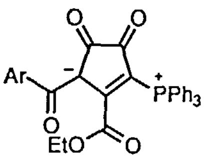

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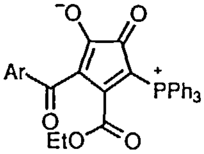

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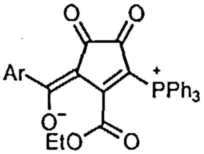

F

β,γ,β′-trioxo ylides,[2] oxalyl diylides,[3] and β,γ-dioxo ylides.[4] The only possible ambiguity is in the region of δ_C 179–186 where there are three doublets and a singlet corresponding to C-1, C-3, C-4 and ArCO.* We have previously noted

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* Note: Throughout this paper atoms numbered C-1, C-2, *etc.* refer to the systematic numbering as shown in the structures of **4** and **5** whereas C(1), C(2), etc. refer to the crystallographic numbering system shown in Figure 1.

that in acyclic ylides containing the $Ph_3P{=}C\text{-}CO\text{-}COR$ grouping the three bond coupling to the γ-carbonyl is greater than the two bond coupling to the β-carbonyl except when R is alkyl,[2,3] although the β,γ,β′,γ′-tetraoxo ylides provide an exception to this pattern.[4] The only comparable cyclic structures previously reported are the deep blue ylide **6** described by Capuano and co-workers,[5]and the trioxo diylide **7** described by Bestmann and co-workers.[6] In the former case no ^{13}C NMR data were obtained but in the latter the observed coupling constants for the COCO carbon signal of 6 and 20 Hz were assigned as $^2J_{P\text{-}C}$ and $^3J_{P\text{-}C}$ respectively, in agreement with our assignment.

TABLE I ^{13}C NMR spectra of 4 and 5

	4		5	
Assignment	δ	$J_{P\text{-}C}$	δ	$J_{P\text{-}C}$
C-1 of P-Ph	121.0	93	121.1	93
C-2 of P-Ph	134.3	11	134.3	11
C-3 of P-Ph	129.3	13	129.3	13
C-4 of P-Ph	133.9	2	133.8	2
P=C (C-5)	72.6	120	71.9	119
C=O (C-4)	184.5	6	184.4	5
C=O(C-3)	182.5	13	182.8	13
C=C (C-2)	111.3	4	111.7	4
C=C (C-1)	179.8	10	179.6	10
*C*O$_2$Et	166.1	2	166.2	2
CO$_2$*C*H$_2$Me	61.8	-	61.8	-
CO$_2$CH$_2$*C*H$_3$	13.3	-	13.4	-
*C*OAr	185.7	-	185.5	-
C-1 of Ar	138.7	-	136.0	-
C-2 of Ar	129.5	-	129.7	-
C-3 of Ar	127.5	-	128.3	-
C-4 of Ar	131.5	-	142.1	-
Me of Ar	-	-	21.7	-

The most remarkable feature of the ^{13}C NMR data is the extreme polarisation of the C-1-C-2 double bond indicated by the Δδ for the two carbons of *ca.* 68 ppm. This parameter has previously been used as a reliable indicator of polarisation in various donor-acceptor substituted alkenes,[7] with values for Δδ of 60–110 ppm being not uncommon.[8] The few previous examples of β,γ-unsaturated phosphonium ylides containing the grouping P=C-C=C-COR for which ^{13}C NMR data have been reported have given signals for the β-carbon at δ_C 140–166 and for the γ-carbon at δ_C 100–124 with Δδ ranging from 32 to 49 ppm.[9] The much greater difference here is clearly due to the β-carbon bearing an ester group which further deshields it to give signals at almost 180 ppm. The possibility for extensive delocalisation of electrons in the ylides **4** and **5** may be represented by the resonance forms **A-F** and the highly shielded nature of C-2 may be taken to indicate a significant contribution from form **D** where it bears a full negative charge.

The contribution of delocalised forms such as **A-F** is associated with different bond orders between the atoms involved and this could be quantified by determining the bond lengths by means of an X-ray structure determination. A suitable crystal of **5** was obtained by slow evaporation of a solution in toluene-dichloromethane and the resulting structure is illustrated in Figure 1. The crystal proved to contain one molecule of toluene of crystallisation per molecule of **5** (not shown) and the position of this was somewhat disordered leading to rather high R values. Nevertheless the observed pattern of bond lengths does provide some evidence for the contribution of the different resonance forms **A-F.** As compared to the bond lengths expected for the conventional representation A,[10] the values obtained for C(5)-O(2), C(4)-O(1), C(2)-C(3) and C(6)-O(3) are higher and those for C(1)-C(5), C(3)-C(4), C(1)-C(2) and C(3)-C(6) are lower, although the differences are in some cases only of marginal statistical significance due to the rather high standard deviations. The value of 1.73 Å for P-C(1) is in the range expected for stabilised ylides,[11] and much greater than the length of 1.66 Å observed for $Ph_3P{=}CH_2$.[12] It is also notable that, in all the possible forms **A-F,** C(4)-C(5) is a single bond and the ester group is unaffected and the observed bond lengths are in agreement with this. In addition to the examples mentioned in ref. 11, there have been several recent X-ray studies on stabilised ylides,[13] and these show that delocalisation as represented by the conversion of form **B** into form **C** is particularly significant. However none of the previous structures examined allow for such extensive delocalisation as is possible in this case. Only Bestmann and co-workers have reported X-ray structures of cyclic polyoxo ylides,[6,14] and the structure of **7**[6] provides a particularly good model for comparison with that of **5.** In fact the bond lengths and angles of the common $Ph_3P{=}C\text{-}CO\text{-}CO$ fragment are almost identical with both structures showing a marked bending of the two adjacent ring carbonyl oxygens towards each other as reflected in the decrease of O(1)-C(4)-C(5) and O(2)-C(5)-C(4) to 121–122 ° and the increase of C(3)-C(4)-O(1) and O(2)-C(5)-C(1) to 130–133 °.

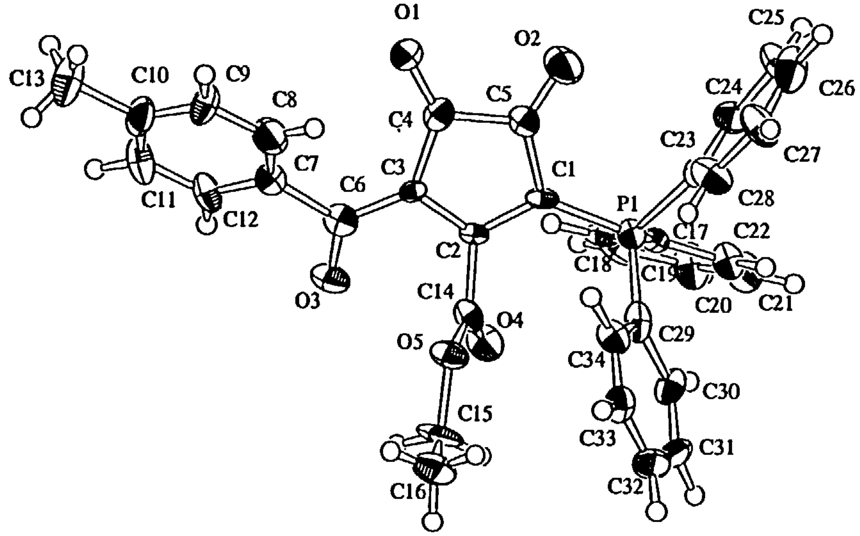

FIGURE 1 X-Ray structure of the delocalised ylide 5 showing crystallographic numbering scheme. Selected bond lengths and angles; C(1)-P(1) 1.73(1), C(1)-C(2) 1.40(2), C(1)-C(5) 1.43(2), C(2)-C(3) 1.37(2), C(2)-C(14) 1.51(2), C(14)-O(4) 1.20(1), C(14)-O(5) 1.32(2), C(3)-C(6) 1.43(2), C(6)-O(3) 1.24(1), C(3)-C(4) 1.46(2), C(4)-O(1) 1.23(1), C(4)-C(5) 1.56(2), C(5)-O(2) 1.24(1) Å; C(1)-C(2)-C(3) 117(1), C(2)-C(3)-C(4) 106(1), C(3)-C(4)-C(5) 103(1), C(4)-C(5)-C(1) 108(1), C(5)-C(1)-C(2) 103(1), C(3)-C(4)-O(1) 133(1), O(1)-C(4)-C(5) 122(1), C(4)-C(5)-O(2) 121(1), O(2)-C(5)-C(1) 130(1) °

It is apparent that in forms **C** and **E** the ylides may adopt a cyclopentadiene structure and this suggested the possibility of a Diels Alder reaction. However the ylides **4** and **5** were recovered unchanged after prolonged treatment with an excess of DMAD and they also failed to undergo Wittig reaction with aromatic aldehydes. Further studies on the reactivity of these highly delocalised ylides are currently in progress.

EXPERIMENTAL

NMR spectra were obtained for ^{13}C at 75 MHz using a Bruker AM300 instrument on solutions in $CDCl_3$ with internal Me_4Si as reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz.

Samples of **4** and **5** were prepared as reported previously[1] and their ^{13}C NMR spectra were determined. The fully assigned spectra are presented in Table I.

X-Ray structure determination

A purple needle crystal suitable for X-ray diffraction was obtained by slow evaporation of a solution in dichloromethane-toluene Crystal data for 5: $C_{41}H_{35}O_5P$ ($C_{34}H_{27}O_5P{\cdot}C_6H_5CH_3$), $M = 638.70$, monoclinic space group $P2_1/n$ (No, 14); a = 19.36(2), b = 9.224(10), c = 20.56(2) Å, β = 114.39(5)°, V = 3344(4) $Å^3$, Z = 4, $D_c = 1.268$ g cm^{-3}, R = 0.099, final $R_w = 0.127$ for 2692 data with $I > 3\sigma(I)$ and 424 parameters. Data were recorded on a Rigaku AFC7S diffractometer at 200 K using Mo-Kα radiation and the structure was solved by direct methods and refined using full-matrix least squares analysis.

Atomic coordinates, molecular dimensions and anisotropic displacement parameters have been deposited in CIF format at the Cambridge Crystallographic Database (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 102/075.

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