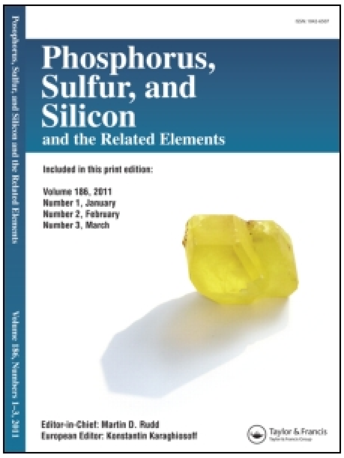

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REACTION OF 1,1,3,3-TETRAKIS(DIMETHYLAMINO)-1λ^5,3λ^5-DIPHOSPHETE, 1, WITH CARBONDISULFIDE II. DIHYDRO-λ^5-PHOSPHETES; NMR ISOTOPE EFFECTS

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REACTION OF 1,1,3,3-TETRAKIS(DIMETHYLAMINO)-1λ^5,3λ^5-DIPHOSPHETE, 1, WITH CARBONDISULFIDE II.† DIHYDRO-λ^5-PHOSPHETES; NMR ISOTOPE EFFECTS

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Dedicated to Professor John G. Verkade on the occasion of his sixtieth birthday

(Received November 28, 1995)

1,1,3,3-Tetrakis(dimethylamino)-1-phospha-3-phosphonium-2-dithio-carboxylato-cyclobutene-1, **2**,[1] is thermally unstable. By heating it is converted quantitatively into [1,1-bis(dimethylamino)-3-thioxo-3,4-dihydro-1λ^5-phosphete-2-yl]-phosphonothioic bis(dimethylamide), **3**. Reaction of the 2,4-dimethylderivative of the title compound **1**, i.e. **4**, with CS_2 yields [1,1-bis(dimethylamino)-2,4-dimethyl-3-thioxo-2,3-dihydro-1λ^5-phosphete-2-yl]-phosphonothioic bis(dimethylamide) **7**. The new compounds are characterized by their properties and their nmr, ir and mass spectra. Isotope effects on $\delta^{31}P$ of **7** are described. The results of the X-ray structural analyses of **3** and **7** are reported and discussed.

Key words: 3-thioxo-3,4-dihydro-1λ^5-phosphete-2-yl, 3-thioxo-2,3-dihydro-1λ^5-phosphete-2-yl, nmr, mass, ir spectra, X-ray structures, nmr isotope effects.

INTRODUCTION

The reaction of CS_2 with 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete, **1**,[2] yields the tetracyclic compound 1,1,3,3-tetrakis(dimethylamino)-1-phospha-3-phosphonium-2-dithio-carboxylato-cyclobutene-1, **2**, as isolable yellow crystals (Equation 1), as reported earlier by us.[1]

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†I. Communication Reference 1.

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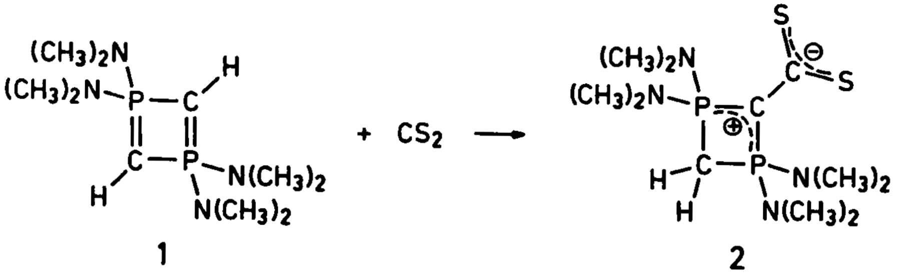
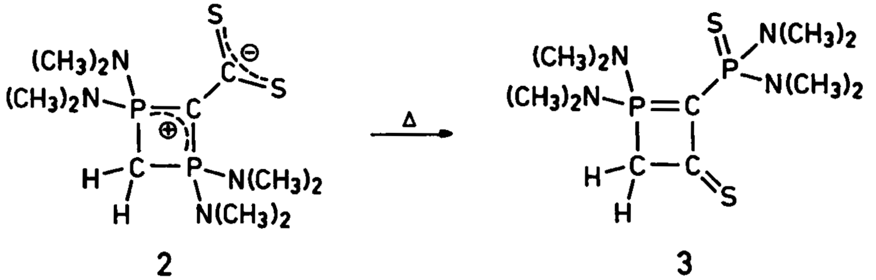

(1)

It was observed that solutions of **2** undergo a change within a few weeks. The results of the investigation of these changes and the problem of the behavior of 2,4-dimethylated λ^5-diphosphete, **4**, in the presence of CS_2 will be dealt with in this report.

THERMAL REARRANGEMENT OF 2 INTO A DIHYDRO-λ^5-PHOSPHETE

The singlet ($\delta^{31}P$ = 26.76 ppm[2]) in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) due to **2** decreased markedly within a few weeks, while the peaks of a new AB spin system at a lower field now became dominant in the spectrum indicating that **2** is thermally not stable. In line with this observation an identical rearrangement was achieved when **2** was heated for two hours to 100°C in a toluene solution. The reaction was quantitative. It was found that the best method for the preparation of the novel compound is to keep **2** for eight hours suspended in boiling tetrahydrofuran. The thermal rearrangement product precipitates in pale yellow cubic crystals from a solution in 1,2-dimethoxyethane at −28°C. According to elemental analysis, mass spectrometroscopic and NMR studies the structure of the product obtained by the thermo-rearrangement of **2** was found to be [1,1-bis(dimethylamino)-3-thioxo-3,4-dihydro-1λ^5-phosphete-2-yl]-phosphonothioic bis(dimethylamide), **3** (see Equation 2). Compound **3** is very soluble in $CHCl_3$, CH_2Cl_2, tetrahydrofuran and toluene, scantily soluble in ether and insoluble in *n*-pentane.


(2)

The E. I. mass spectrum of **3**, which is partially given in Table I, shows the molecular peak with a great intensity (64%). Not clear until now, however, is whether the formation of a new endocyclic C—C bond proceeds by an intra- or intermolecular process.

TABLE I

Abstracts of the E.I. mass spectrum of **3** (70 eV; 370 K)

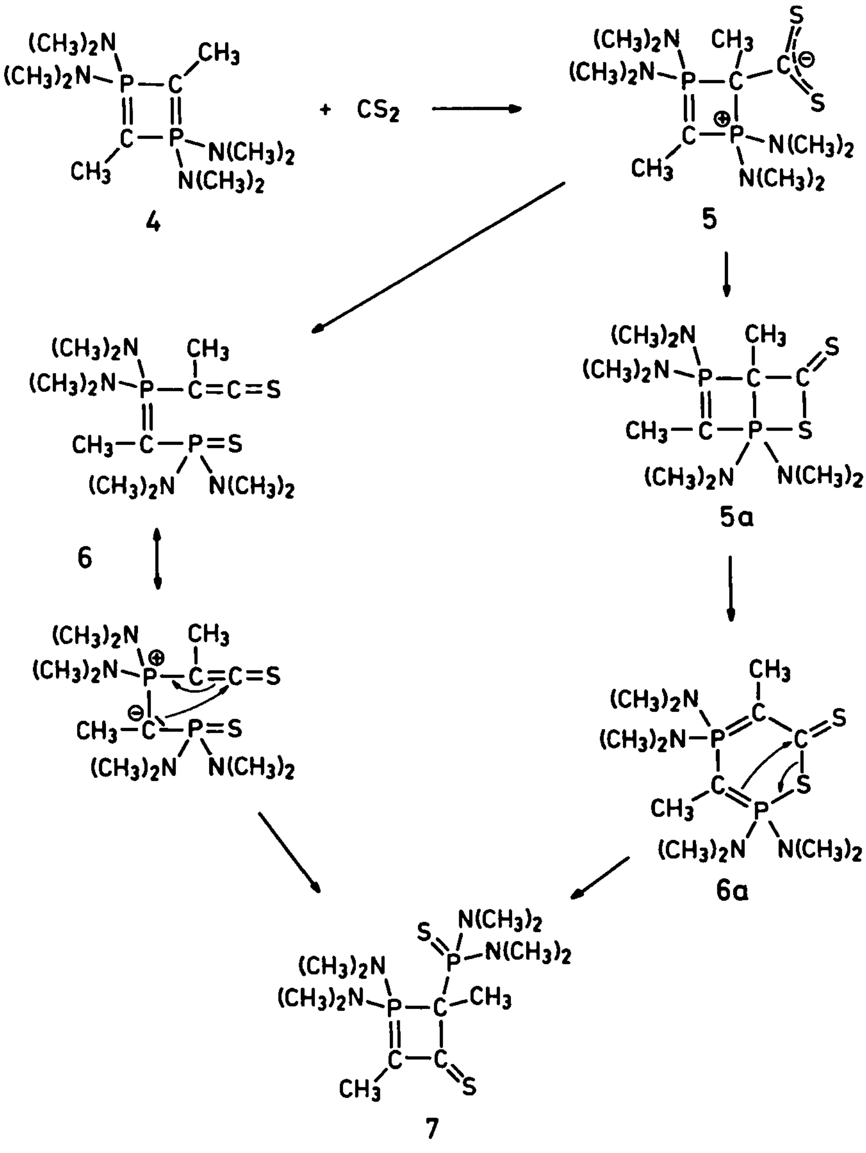
m/e	Rel. Intensity (%)	Fragment
340	64.0	M^+
296	5.6	$[M - Nme_2]^+$
252	100.0	$[M - 2\,Nme_2]^+$
209	13.0	$[M - 3\,Nme_2 + H]^+$
151	10.2	$[SP(Nme_2)_2]^+$
145	12.4	$[M - SP(Nme_2)_2 - Nme_2]^+$
119	66.0	$[P(Nme_2)_2]^+$
76	45.2	$[HP(Nme_2)]^+$
58	22.9	$[CH_2CS]^+$
44	35.3	$[Nme_2]^+$

REACTION OF 1,1,3,3-TETRAKIS(DIMETHYLAMINO)-2,4-DIMETHYL-1λ^5,3λ^5-DIPHOSPHETE 4 WITH CARBONDISULFIDE

Since the formation of **2** from **1** and carbon disulfide occurs through a proton migration of a methylene group, the question arose how carbon disulfide would react with the dimethylated diphosphete **4**[3] because due to the methyl groups in the 2- and 4-position of **4**, the formation of a product similar to **2** according to Equation 1 as well as of a 3,4-dihydro-1λ^5-phosphete-2-yl-phosphonothioacid derivative is precluded.

Upon addition of carbon disulfide to a solution of **4** at −70°C and slowly warming up to room temperature development of an orange color was observed. The $^{31}P\{^1H\}$ NMR spectrum showed that only one product was formed. It exhibits an AB spin system with the chemical shift of $\delta^{31}P = 62.6$ and 83.6 ppm with a small P—P coupling constant of only 0.4 Hz ($CDCl_3$). From this solution [1,1-bis(dimethylamino)-2,4-dimethyl-3-thioxo-2,3-dihydro-1λ^5-phosphete-2-yl]-phosphonothioic bis(dimethylamide), **7**, could be isolated in a good yield.

It is assumed that during the first reaction step between earlier described **4**[3] and CS_2 a nucleophilic endocyclic carbon atom formed the bond to the C-atom of the CS_2 to yield **5** as the primary product (see Scheme I) as it is generally the case in reactions between phosphorylides and CS_2.[4-6] This reaction type also was observed during the interactions of CS_2 and **1** (see Equation 1).[1] However, according to the $^{31}P\{^1H\}$ NMR spectrum of a mixture consisting of **4** and CS_2, signals which could be attributed to such a compound were missing. It was observed, however, that at temperature depending $^{31}P\{^1H\}$ NMR measurements on such a mixture in toluene-d_8, at 190 K no reaction between these two components took place. However, after 5 minutes at 213 K lines of an AB spin system in the region of 63 to 69 ppm with a concomitant P—P coupling constant of 108.7 Hz appeared. It is conceivable, though not definitely assured, that these signals are caused by the acyclic intermediate **6**, from which eventually the stable end product **7** of this reaction as racemate of two enantiomeric forms is produced (see X-ray structure of **7**). The



SCHEME I

AB spin system, however, also could be due to a six-membered intermediate **6a**, which was produced from **5** via the bicyclic system **5a** leading finally to formation of **7**. An analogous mechanism was already earlier suggested by us for the reaction of **4** with COS and CO_2 also resulting in the formation of dihydro-λ^5-phosphetes.[7]

Compound **7** is very soluble in $CHCl_3$ and CH_2Cl_2, soluble in toluene, diglyme, and tetrahydrofuran, slightly soluble in ether and insoluble in *n*-pentane. Its E.I. mass spectrum is partially reported in Table II. The molecular peak appears with an intensity of 23.6%.

TABLE II

Abstracts of the E.I. mass spectrum of **7** (70 eV; 337 K)

m/e	Rel. Intensity (%)	Fragment
368	23.6	M^+
335	26.5	$[M - SH]^+$
323	6.7	$[M - Nme_2 - H]^+$
279	6.6	$[M - 2Nme_2 - H]^+$
218	22.4	$[M - SP(Nme_2)_2 + H]^+$
217	10.7	$[M - SP(Nme_2)_2]^+$
175	12.6	$[M - SP(Nme_2)_2 - Nme_2 + 2H]^+$
173	8.6	$[M - SP(Nme_2)_2 - Nme_2]^+$
151	26.7	$[SP(Nme_2)_2]^+$
119	100.0	$[P(Nme_2)_2]^+$
76	51.7	$[HPNme_2]^+$
44	30.3	$[Nme_2]^+$

NMR SPECTRA OF THE DIHYDRO-λ^5-PHOSPHETE 3 AND 7

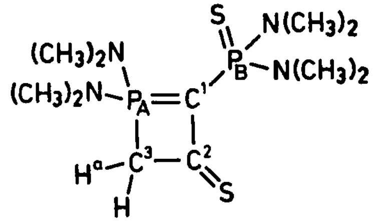
The $^{31}P\{^1H\}$ NMR spectra of **3** and **7** consist of an AB spin system whose chemical shifts can unambiguously be attributed via ^{13}C-satellites to the phosphorus atoms P_A and P_B (see Table III). The endocyclic phosphorus atoms P_A of the 3-thioxo dihydro-$1\lambda^5$-phosphetes **3** and **7** and those of the corresponding 3-oxo-tetracyclic compounds **8** and **9**[7] differ only among their $\delta^{31}P$ values by 6.5 or 6.9 ppm, respectively, with the 3-thioxo derivatives shifting downfield. For the phosphorus atoms P_B of the diaminothiophosphoryl groups only small differences for the $\delta^{31}P$ values (+0.4 or −1.5 ppm, respectively; see Reference 8) were observed. From the values of the $^2J(PP)$ coupling constants of **3** and **7** the position of the P=C-double bonds in the two four-membered heterocycles could be determined, because a geminal PP coupling constant of 45.5 Hz is in agreement with a $P^V{=}C{-}P^V$ fragment (**3**) and one of 0.4 Hz is indicative for a $P^V{-}C{-}P^V$ triade containing a sp^3-hybridized carbon atom (**7**).[9-12]

In the $^{13}C\{^1H\}$ NMR spectra of **3** and **7** the position of the P=C double bonds of the tetracycles is recognizable by the reversed values of the $^1J(P_AC^1)$ and $^1J(P_AC^3)$ coupling constants, with the larger of the two values to be attributed to the P=C-bonds.[10,11] These values are about twice as large as the $^1J(PC)$-values of the endocyclic PC-single bonds of **3** or **7**, respectively. A value for $\delta^{13}C^2$ in both rings was found to be close to the one for carbon disulfide (192.8 ppm).[13] The $\delta^{13}C$-values of the sp^2-hybridized carbon atoms C^1 of **3** and C^3 of **7** differ hardly (0.8 ppm; see Table III) from each other and exhibit a downfield shift of 29.0 and 32.6 ppm relative to those of the corresponding 3-oxo-dihydro-$1\lambda^5$-phosphetes **8** and **9**. Of note are the different vicinal P_BC^3-coupling constants of **3** and **7** (29.1 and 13.1 Hz, respectively), which show a dependency of the vicinal P_BC^3-coupling of the dihedral angle of $P_B{-}C^1{-}P_A{-}C^3$.[14]

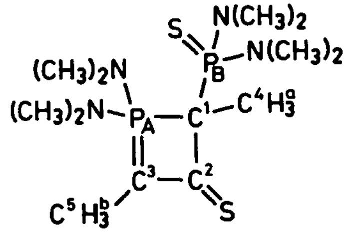
The methylene carbon atom C^3 of **3** and the quaternary endocyclic C-atoms of the

TABLE III

NMR parameters of **3** and **7** in $CDCl_3$ at 300 K



3



7

δ/ppm				^nJ/Hz; n = 1 - 5			
		3	7			3	7
^{31}P:	P_A	55.1	62.4	n = 1:	P_AC^1	137.2	55.7
	P_B	63.7	83.5		P_AC^3	66.0	113.1
$^{13}C^{\alpha}$:	C^1	114.2	82.4		P_BC^1	91.6	90.9
	C^2	195.0	193.6		$P_A{}^{15}N^{1,2}$		22.1^{β}
							8.9
	C^3	46.6	113.4		$P_B{}^{15}N^{1,2}$		17.5^{β}
							17.1
	C^4	-	21.5	n = 2:	P_AP_B	45.5	0.4
	C^5	-	11.3		$P_{A,B}C^2$	6.5^{β}	6.1 (P_A)
^1H:	H^a	γ	1.956			1.5	9.4 (P_B)
	H^b	-	1.971		P_AC^4	-	9.6
					P_BC^4	-	4.1
					P_AC^5	-	4.0
				n = 3:	P_BC^3	29.1	13.1
					$P_{A,B}H^{a\,\beta}$		17.5
						γ	19.9
					P_AH^b	-	16.8
				n = 5:	P_BH^b	-	4.0

α: $\delta^{13}C$ in ppm of $N(CH_3)_2$ groups ($^2J(PC)$ in parentheses): 36.5 (4.3 Hz); 37.0 (4.5 Hz) (**3**); 37.8 (3.9 Hz); 39.6 (<0.3 Hz); 40.3 (0.7 Hz); 40.5 (3.7 Hz) (**7**); β: not assigned; γ: $^1H^a$ signals hidden under lines of dimethylamino groups (2.4 - 3.2 ppm).

two rings were identified by ^{13}C-DEPT spectroscopy. Due to the asymmetric carbon atom C^1 of **7** four different $\delta^{13}C$ and δ^1H values of the dimethylamino groups were found; the corresponding geminal PC coupling constants differ considerably from each other (see Table III). The diasterotopic dimethylamino substituents at the exocyclic phosphorus atom P_B of **7** possess two $^1J(P^{15}N)$ couplings which differ only by 0.4 Hz; these absolute values were obtained from the ^{15}N satellites of the $^{31}P\{^1H\}$ NMR spectrum (see Figure 1) and appear in the region to be expected for amino-

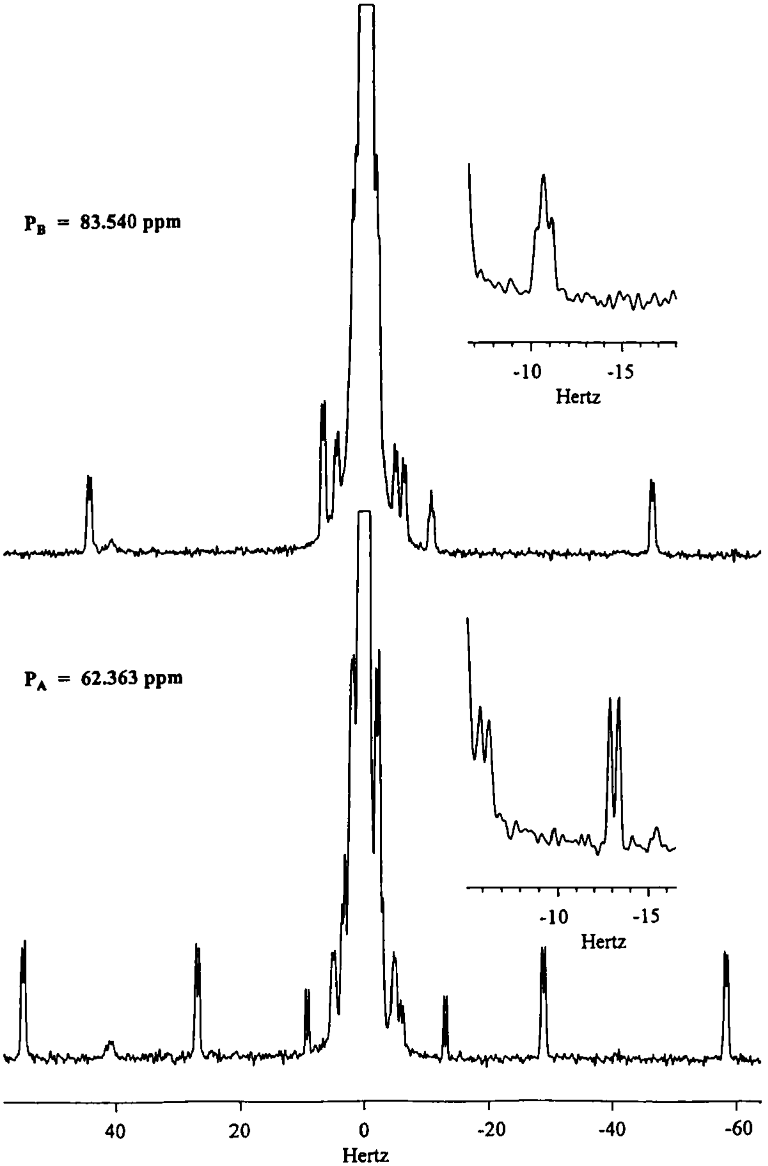


FIGURE 1 ^{13}C and ^{15}N satellites in the 101.256 MHz $^{31}P\{^1H\}$ NMR spectrum of the endocyclic phosphorus atoms P_A (below) and the exocyclic P_B (above) of 2-thiophosphoryl substituted 2,3-dihydro-1λ^5-phosphete 7 in C_6D_6 at 300 K (see Table III, where the phosphorus atoms are identified; 12,000 scans; digital resolution 0.03 Hz per point; total experimental time 14.4 h). The expanded split signals are individual low frequency parts of the ^{15}N satellites of the phosphorus atoms P_A and P_B, respectively (see text).

thiophosphoryl groups.[15] In contrast the $^1J(P^{15}N)$ values of the two P_A anisochronic nitrogen atoms are markedly different from each other (factor 2.5).

The $^{31}P\{^1H\}$ NMR spectrum of the dihydro-λ^5-phosphete 7 (see Figure 1) permits on the basis of the satellites belonging to the [mono-$^{13}C^i$]- (i = 1–5) and to the four [mono-^{15}N] isotopomers to attribute all ^{13}C and ^{15}N isotope effects relative to the

TABLE IV

One-, two- and three-bond isotope shifts ${}^n\Delta^{31}P({}^{13}C)$, n = 1–3, and ${}^1\Delta^{31}P({}^{15}N^{1,2})$ of P_A and P_B of **7** (ppb)[α] in $CDCl_3$ at 300 K (for atomic numbering see Table III and Fig. 1)

Isotope Shift	P_A	P_B
${}^1\Delta^{31}P({}^{13}C^i)$		
i = 1	-10	-10
i = 3	-18	-
${}^2\Delta^{31}P({}^{13}C^i)$		
i = 2	+4	-3
i = 4	-1	-2
i = 5	-2	-
${}^3\Delta^{31}P({}^{13}C^3)$	-	+2
${}^1\Delta^{31}P({}^{15}N^{1,2})$	-21[β]	~ -20[β]
	-17	~ -20

α: ${}^{13}C$ and ${}^{15}N$ induced isotope shifts (10^{-9}) over one (${}^1\Delta$), two and three bonds (${}^2\Delta$, ${}^3\Delta$) for ${}^{31}P_A$ and ${}^{31}P_B$ relative to the [per-^{12}C]isotopomer and the [per-^{14}N]isotopomer, respectively (± 1 ppb). β: No assignment of the two different ${}^1J({}^{31}P_A{}^{15}N)$ and ${}^1J({}^{31}P_B{}^{15}N)$ coupling constants to the individual dimethylaminogroups was possible, respectively (see text).

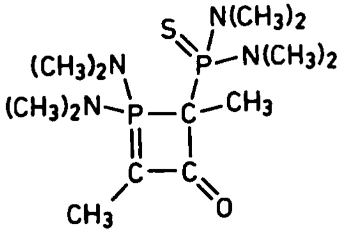
chemical shifts $\delta^{31}P_A$ and $\delta^{31}P_B$ of the [per-^{12}C]isotopomer or the [per-^{14}N]isotopomer, respectively (see Table IV). Because of the geminal P_AP_B coupling (0.4 Hz) all the satellite peaks occur as doublets. The carbon atoms which are linked directly to P_A and P_B cause, as expected, isotope shifts ${}^1\Delta\ {}^{31}P({}^{13}C^i)$, i = 1 and 3, to higher fields[16,17]; they appear in the region of the ${}^1\Delta^{31}P({}^{13}C)$ values as observed for $1\lambda^5,3\lambda^5$-diphosphabenzenes (λ^5-diphosphinines)[12] and 1,4-dihydro-$1\lambda^5,4\lambda 5$-diphosphabenzenes.[18] The values of ${}^1\Delta^{31}P({}^{15}N^{1,2})$ of the dimethylamino groups of P_A and P_B of **7** and the aminosubstituents at the four-coordinated phosphorus of several 2-phenylamino-4-methyl-1,3,2-dioxaphosphorinanes with identical sign are similar with each other (12.1–21 ppb).[15] At the endocyclic phosphorus atom P_A the ${}^1\Delta^{31}P({}^{15}N^{1,2})$ values and also the two ${}^1J(P^{15}N)$ values are distinctly different, while at the exocyclic P_B these two parameters are almost identical (see above and Table IV).

Comparing the ${}^1\Delta^{31}P({}^{15}N)$ shifts of **7** with those of a number of di- and triazaphospholes with di-coordinated phosphorus,[19] it becomes evident that the last ones are significantly larger (factor = 4–6). A corresponding dependency of the coordination number of the phosphorus was also determined at ${}^1\Delta^{31}P({}^{13}C)$. At a dianionic $2\sigma^2,4,6\sigma^2,8$-tetraphosphapentalene derivative we were able to determine the isotope shift of the $\sigma^2\lambda^3$-phosphorus atoms by the directly adjacent carbon atom to −64 ppb.[20] An interpretation concerning the ${}^1\Delta^{31}P$ findings is presently due to scarity of data not possible.

The induced isotope effects ${}^{2}\Delta^{31}P_{A,B}({}^{13}C)$ through two bonds due to the ${}^{13}C$ atoms of the methylene groups of **7**, as of ${}^{1}\Delta^{31}P$, are for the heavier isotopomers, as expected, shifted to higher fields (see Table IV).[16,17] Noteworthy in connection with this observation is that the endocyclic ${}^{13}C^{2}$ atom shifts the lines of the exocyclic ${}^{31}P_{B}$, as expected, upfield, while the lines of the endocyclic ${}^{31}P_{A}$ are shifted by 4 ppb into the opposite direction. Positive ${}^{2}\Delta^{31}P({}^{13}C)$ isotopic shifts are also known for *trans*-ethene-1,2-bis(dialkyl-phosphonates)[21]; in addition there exists a report of a positive value of the ${}^{2}\Delta^{13}C({}^{13}C)$-values of the carbonyl carbon atom in cyclobutanone.[22] The isotope effect as determined by us at the [mono-${}^{13}C^{3}$] isotopomer of **7** through three bonds ${}^{3}\Delta^{31}P_{B}({}^{13}C^{3})$ is with a value of +2 ppb also positive.

MOLECULAR AND CRYSTAL STRUCTURE OF 3 AND 7

Table V contains the crystallographic data to the solutions of structures, Table VI selected bond lengths, Table VII selected bond angles, and Tables VIII and IX the atom coordinates of **3** and **7**, respectively. For comparison in Tables VI and VII are included some bond lengths and bond angles of the 3-oxo-dihydro-1λ^{5}-phosphete **9**—the O-analogue of **7**—and the dihydro-1λ^{5}-phosphete **10**,[7] which is the O-analog of **9**.



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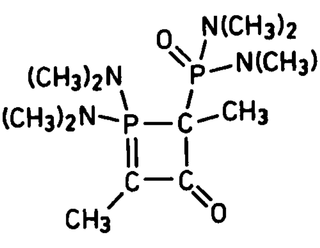

10

Figures 2 and 3 represent SCHAKAL projections[25] of **3** and of one species of **7**, in which three independent, but almost superimposable molecules, occur in the asymmetric unit. Both compounds contain, within the standard deviation, planar PC_3-skeletons, in which two of the carbon atoms (C3 and C4) are sp^2- and one (C2) is sp^3-hybridized. The bonding relationships have been discussed in detail for the analogous compounds which possess instead of a sulfur atom at the endocyclic carbon atom an oxygen atom (**9**) or both sulfur atoms are replaced by oxygen atoms (**10**), respectively.[7] Remarkable is the very short bond Pl—C4 (174 pm average value

TABLE V

Crystal parameters and details of structure determination of **7** and **3**

	7	**3**
Lattice constants	a = 3348,0(7)pm b = 1331,0(3)pm c = 1339,1(3)pm β = 100,97°	a = 914,7(2)pm b = 1246,6(2)pm c = 1589,5(3)pm
Unitcell volume	5858 Å^3	1812 Å^3
Formula units	12	4
Density (calculated)	1,25 g/cm^3	1,25 g/cm^3
Crystal system; space group	monoclinic; $P2_1/c$	orthorhombic; $P2_12_12_1$
Diffractometer used	Four circle diffractometer CAD4	
Radiation	Cu-Kα (graphite monochromator)	
Temperature	20°C	
Selected reflections for determination of unit cell constants	25	
Measuring range; procedure	2,3° < Θ < 26,7°, ω-scans	
Number of		
a) measured reflections	7979	3044
b) independent reflections	7195	2687
c) unobserved reflections	4524 (Fo < 5σ(Fo))	1975 (Fo < 4σ(Fo))
Corrections	Lorentz and polarization factor; empirical absorption correction, $\mu = 40\ \text{cm}^{-1}$	Lorentz and polarization factor; empirical absorption correction, $\mu = 46\ \text{cm}^{-1}$
Structure solution	Direct methods	
Refinement method	Least squares	
Restrictions	CH_3 groups with H-C-H 109,5° and C-H 96 pm	CH_3 and CH_2 groups with H-C-H 109,5° and C-H 96 pm
Programs used	SHELXTL-PLUS [23] PLATON [24] SCHAKAL[25]	
Scattering factors	International Tables Vol. C, 1992, p. 476	
$R = \Sigma \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \Sigma\lvert Fo\rvert$	0.059	0.04
$wR = (\Sigma(w(\lvert Fo\rvert - \lvert Fc\rvert))^2 / \Sigma(w\lvert Fo\rvert)^2)^{0,5}$	0.044	0.029

for **7** and 173.6 pm for **3**) and the prolonged CC single bonds C2—C21 (153 pm for **7**) and C2—C3 (156 pm for **7** and 152.6 pm for **3**). These facts point to a very strained ring system and to an electron delocalization extending between the multiple bonds (C3—C4 137 pm and 139.5 pm) (see Table VI).

Comparing the bond angles of the four-membered ring (see Table VII) with those of the above mentioned compounds **9** and **10** indicates, that the rings are distorted analogously to the ones in λ^3-dihydrophosphetes.[26] This is obviously only a function of the bonding relationships and the hybridization of the four-membered ring: the smallest angle is formed by the two longest bonds (C2—P1—C4 79.7°, average

TABLE VI

Selected bond lengths [pm] of 3-thioxo-dihydro-1λ^5-phosphetes **3** and **7**. By comparison, the dihydro-1λ^5-phosphetes **9** and **10**[7] are given (see text).

	7A	7B	7C	3	9	10
P2 - S2	194,8(3)	195,8(3)	195,0(3)	195,5(2)	192,9(1)	------
P2 - N	165,0/ 162,0(6)	164,9/ 162,1(7)	164,1/ 163,2(6)	164,0/ 165,7(4)		------
P2 - C2	186,2(7)	184,6(7)	182,5(7)	------	183,0(2)	182,1(2)
C2 - C21	154(1)	153(1)	155(1)	------	153,0(3)	154,0(3)
P1 - N	165,4/ 162,0(6)	163,8/ 162,1(7)	162,3/ 164,4(7)	162,5/ 162,8(4)		------
P1 - C2	184,8(7)	184,9(7)	187,3(7)	180,7(5)	186,3(2)	184,9(2)
P1 - C4	174,8(7)	173,3(7)	173,7(7)	173,6(5)	170,8(2)	170,9(2)
C2 - C3	156(1)	157(1)	153(1)	152,6(7)	159,1(3)	158,7(3)
C3 - C4	136(1)	135(1)	139(1)	139,5(6)	139,6(3)	139,1(3)
C4 - C41	149(1)	148(1)	148(1)	------	149,8(3)	149,9(3)
C3 - S1	169,0(8)	170,1(7)	170,6(8)	166,5(5)	------	------

TABLE VII

Selected bond angles [°] of 3-thioxo-dihydro-1λ^5-phosphetes **3** and **7**. By comparison, the dihydro-1λ^5-phosphetes **9** and **10**[7] are given (see text).

	7A	7B	7C	9	10		3
S2-P2-C2	107,9(2)	107,4(3)	107,3(3)			S2-P2-C4	108,7(2)
P2-C2 C3	127,1(5)	126,5(5)	127,1(5)			P2-C4-C3	138,0(4)
P2-C2-C21	106,6(5)	108,0(5)	106,7(5)				
P1-C2-C21	116,0(5)	115,3(5)	116,6(5)				
P1-C2-P2	111,8(4)	113,0(4)	113,7(4)			P1-C4-P2	129,1(3)
P1-C4-C41	135,9(6)	136,1(6)	136,9(6)				
C3-C4-C41	130,0(7)	130,0(7)	131,5(7)				
C21-C2-C3	110,8(6)	109,8(6)	109,9(6)				
S1-C3-C2	127,6(6)	127,0(6)	125,0(5)			S1-C3-C2	124,1(3)
S1-C3-C4	128,5(6)	128,7(6)	128,9(6)			S1-C3-C4	134,0(4)
C2-P1-C4	79,2(3)	79,9(3)	81,2(3)	81,42(9)	81,5(1)		79,6(2)
P1-C2-C3	83,6(4)	82,6(4)	81,7(4)	82,2(1)	82,3(1)		85,9(3)
C2-C3-C4	103,2(6)	103,9(6)	105,6(6)	102,4(2)	102,4(2)		101,8(4)
C3-C4-P1	93,9(5)	93,6(5)	91,5(5)	94,0(1)	93,6(1)		92,8(3)

value in **7**, and 79.6° in **3**); of the two intermediate size angles P—C—C, naturally the one at the sp^2-hybridized C-atom is larger (Pl—C2—C3 82.6° in **7** and 85.9° in **3**; Pl—C4—C3 93.0° in **7** and 92.8° in **3**). The largest bond angle is situated between the shortest bonds (C2—C3—C4 104.2° in **7** and 101.8° in **3**).

The chiral compound **7**, because of the centrosymmetry of the space group $P2_1/c$ has been found to occur as a racemate, while **3** crystallizes in the acentric space group $P2_12_12_1$. The result of refinement of Roger's parameter[23] points for **3** to be in the prescribed configuration.

TABLE VIII

Atomic coordinates and equivalent isotropic thermal parameters U_{eq} [Å^2] for compound **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}-tensor.

Atom	x	y	z	U_{eq}
S1	0.3597(2)	0.3186(1)	0.31411(8)	0.0594(6)
S2	0.0209(2)	0.6754(1)	0.40664(8)	0.0577(5)
P1	-0.0480(2)	0.4003(1)	0.36280(7)	0.0420(5)
P2	0.1887(1)	0.5782(1)	0.40458(7)	0.0383(4)
N11	-0.1327(4)	0.3816(3)	0.4515(2)	0.054(2)
N12	-0.1706(5)	0.4448(3)	0.2973(3)	0.055(2)
N21	0.2633(4)	0.5677(3)	0.4980(2)	0.048(2)
N22	0.3264(4)	0.6104(3)	0.3417(2)	0.043(1)
C2	0.0545(5)	0.2880(3)	0.3215(3)	0.048(2)
C3	0.1899(5)	0.3568(3)	0.3368(3)	0.043(2)
C4	0.1287(5)	0.4502(3)	0.3700(3)	0.036(2)
C111	-0.2661(6)	0.3168(5)	0.4548(3)	0.079(3)
C112	-0.0766(7)	0.4168(5)	0.5312(3)	0.085(3)
C121	-0.1332(7)	0.4512(5)	0.2082(3)	0.087(3)
C122	-0.2837(6)	0.5213(5)	0.3227(4)	0.082(3)
C211	0.2225(6)	0.6274(4)	0.5723(3)	0.061(2)
C212	0.3859(6)	0.4948(5)	0.5102(3)	0.079(3)
C221	0.3030(6)	0.6035(5)	0.2514(3)	0.064(2)
C222	0.4097(6)	0.7061(5)	0.3658(4)	0.075(3)

EXPERIMENTAL

All reactions were performed under careful exclusion of moisture in an atmosphere of dried and repurified argon. Solvents were dried according to known procedures and were saturated with argon.

The NMR spectra were obtained by a AC 250 NMR spectrometer (Bruker Analytische Meßtechnik GmbH, Rheinstetten; ^{1}H: 250.133 MHz). 85% aqu. Orthophosphoric acid was used as external standard for δ^{31}P chemical shifts. Tetramethylsilane (TMS) was used as internal standard for obtaining δ^{13}C and δ^1H shifts. As usual, positive shift values signify downfield shifts.

For measurements of the mass spectra a MAT 711 (Varian) was used and for obtaining the IR spectra a Perkin-Elmer IR spectrophotometer 883 with an CDS data station was employed.

[1,1-Bis(dimethylamino)-3-thioxo-3,4-dihydro-1λ^5-phosphete-2-yl]-phosphonothioic bis-(dimethylamide), **3**: An amount of 2 g (5.9 mmol) of 1,1,3,3-tetrakis(dimethylamino)-1-phospha-3-phosphonium-2-dithio-carboxylato-cyclobutene-1, **2**[1] was suspended in 50 ml tetrahydrofuran and refluxed for 8 hours. After cooling the clear, orange colored solution to room temperature, the solvent was evaporated under vacuum. The formed residue was dissolved in 10 ml DME. Yellow crystals of **3** precipitated from this solution when cooling to −28°C. Upon repeated concentration of the mother liquor a second fraction was obtained, m.p. 143°C, yield 1.6 g (79.7%). Anal.: Calcd. for $C_{11}H_{26}N_4P_2S_2$ (Mol. Wt. 340.4): C, 38.81; H, 7.70; N, 16.46. Found C, 38.16; H, 7.97; N, 16.06. MS (see Table I); IR, Nujol slurry between CsBr plates (in cm^{-1}): 1367 s, 1348 s, 1291 s, 1190 sh, 1170 vs, 1145 sh, 1091 m, 1064 m, 1039 w, 1017 s, 990 sh, 980 vs, 964 s, 874 s, 855 s, 759 vs, 647 s, 618 vs, 543 vw, 506 vw, 482 m, 435 w, 378 w, 338 vw (vs = very strong, s = strong, m = middle, w = weak, vw = very weak, sh = shoulder).

(1,1-Bis(dimethylamino)-2,4-dimethyl-3-thioxo-2,3-dihydro-1λ^5-phosphete-2-yl)-phosphonothioic bis(dimethylamide) **7**: A solution of 0.3 g (4 mmol) carbon disulfide in 5 ml toluene is slowly added at −70°C to a stirred solution of 1 g (3.4 mmol) 1,1,3,3-tetrakis(dimethylamino)-2,4-dimethyl-1λ^5,3λ^5-diphosphete **4**[3] in 5 ml toluene and brought to room temperature (ca. 6 hrs). Toluene is distilled off under vacuum from the obtained orange-yellow solution to leave an oily residue which is dissolved in ca. 5 ml DME. After keeping for about 3 days at −32°C pure crystals of **7** are obtained: concentrating the mother liquors results in additional **7**; m.p. 162°C; yield 0.8 g (63.8%). Anal.: Calcd. for $C_{13}H_{30}N_4P_2S_2$ (Mol. Wt. 368.5): C, 42.37; H, 8.21; N, 15.20. Found C, 42.47; H, 8.35; N, 15.05. MS (see Table II);

TABLE IX

Atomic coordinates and equivalent isotropic thermal parameters U_{eq} [Å^2] for the three crystallographically independent molecules of compound 7. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}-tensor.

Atom	x	y	z	U_{eq}
S1A	0.45242(7)	0.7179(2)	0.3499(2)	0.068(1)
S2A	0.38631(7)	0.3332(2)	0.1886(2)	0.051(1)
P1A	0.37185(6)	0.5065(2)	0.3795(2)	0.0339(7)
P2A	0.42704(6)	0.4362(1)	0.2343(2)	0.0338(8)
N11A	0.3792(2)	0.4043(4)	0.4510(5)	0.041(3)
N12A	0.3233(2)	0.5204(4)	0.3413(5)	0.043(3)
N21A	0.4477(2)	0.4749(4)	0.1387(5)	0.046(3)
N22A	0.4607(2)	0.3956(5)	0.3323(5)	0.043(3)
C111A	0.3536(3)	0.3141(6)	0.4270(7)	0.061(4)
C112A	0.4157(2)	0.3876(6)	0.5246(6)	0.051(4)
C121A	0.2977(3)	0.5457(7)	0.4133(7)	0.071(4)
C122A	0.2996(2)	0.4824(7)	0.2443(6)	0.062(4)
C211A	0.4567(3)	0.4046(6)	0.0626(7)	0.074(4)
C212A	0.4705(3)	0.5677(6)	0.1396(7)	0.078(5)
C221A	0.4716(3)	0.2880(6)	0.3409(7)	0.067(4)
C222A	0.4976(3)	0.4555(7)	0.3650(7)	0.076(4)
C21A	0.3763(2)	0.5972(5)	0.1872(5)	0.043(3)
C2A	0.4009(2)	0.5448(5)	0.2815(5)	0.028(3)
C3A	0.4200(2)	0.6237(5)	0.3632(6)	0.042(3)
C4A	0.3996(2)	0.6077(5)	0.4402(6)	0.038(3)
C41A	0.4001(3)	0.6662(6)	0.5357(6)	0.056(4)
S1B	0.23724(7)	0.2580(1)	0.8291(2)	0.060(1)
S2B	0.26423(7)	0.6788(2)	0.9406(2)	0.067(1)
P1B	0.29647(6)	0.5031(2)	0.7741(2)	0.0380(8)
P2B	0.23470(7)	0.5520(2)	0.9108(2)	0.0407(8)
N11B	0.2833(2)	0.5977(5)	0.6966(5)	0.054(3)
N12B	0.3452(2)	0.5103(5)	0.8137(5)	0.051(3)
N21B	0.2185(2)	0.5111(5)	1.0117(5)	0.055(3)
N22B	0.1982(2)	0.5647(5)	0.8119(5)	0.051(3)
C111B	0.3050(3)	0.6948(6)	0.7085(7)	0.080(5)
C112B	0.3654(3)	0.5695(7)	0.9018(7)	0.075(5)
C121B	0.3728(3)	0.4696(8)	0.7534(8)	0.096(5)
C122B	0.2027(3)	0.5817(7)	1.0788(7)	0.085(5)
C211B	0.2050(3)	0.4087(6)	1.0226(7)	0.074(4)
C212B	0.1710(3)	0.4812(7)	0.7795(8)	0.076(5)
C221B	0.1749(3)	0.6596(7)	0.7940(8)	0.094(5)
C222B	0.2991(2)	0.4258(5)	0.9746(5)	0.045(3)
C21B	0.2707(2)	0.4591(5)	0.8766(5)	0.032(3)
C2B	0.2599(2)	0.3669(5)	0.8037(6)	0.039(3)
C3B	0.2770(2)	0.3898(5)	0.7229(6)	0.040(3)
C4B	0.2440(3)	0.6014(7)	0.6271(6)	0.071(4)
C41B	0.2797(3)	0.3295(6)	0.6314(6)	0.067(4)

TABLE IX (*Continued*)

Atom	x	y	z	U_{eq}
S1C	0.09795(7)	0.6638(2)	0.1769(2)	0.061(1)
S2C	0.06775(7)	0.3569(2)	0.4568(2)	0.060(1)
P1C	0.05662(6)	0.3864(2)	0.1889(2)	0.0391(8)
P2C	0.09596(6)	0.4661(2)	0.4022(2)	0.0413(8)
N11C	0.0084(2)	0.3608(4)	0.1594(5)	0.045(3)
N12C	0.0814(2)	0.2793(4)	0.2058(5)	0.045(3)
N21C	0.1417(2)	0.4354(5)	0.3867(5)	0.045(3)
N22C	0.0988(2)	0.5661(5)	0.4785(5)	0.053(3)
C111C	-0.0059(3)	0.3173(7)	0.0576(7)	0.072(4)
C112C	-0.0201(2)	0.3552(6)	0.2282(7)	0.064(4)
C121C	0.0640(3)	0.1903(5)	0.2466(7)	0.066(4)
C122C	0.1243(2)	0.2719(6)	0.1996(7)	0.064(4)
C211C	0.1659(3)	0.3734(7)	0.4720(7)	0.078(5)
C212C	0.1680(2)	0.4874(6)	0.3297(7)	0.063(4)
C221C	0.1224(3)	0.6537(6)	0.4586(8)	0.084(5)
C222C	0.0741(3)	0.5776(6)	0.5571(6)	0.067(4)
C21C	0.0665(2)	0.4969(5)	0.2768(5)	0.033(3)
C2C	0.0828(2)	0.5421(5)	0.1853(6)	0.040(3)
C3C	0.0771(2)	0.4678(5)	0.1107(6)	0.041(3)
C4C	0.0292(2)	0.5560(5)	0.2943(6)	0.048(3)
C41C	0.0844(3)	0.4676(6)	0.0055(6)	0.066(4)

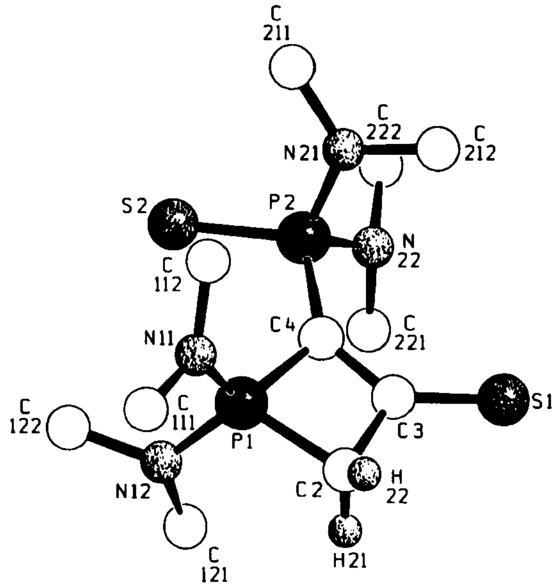

FIGURE 2 Molecular structure of compound 3.

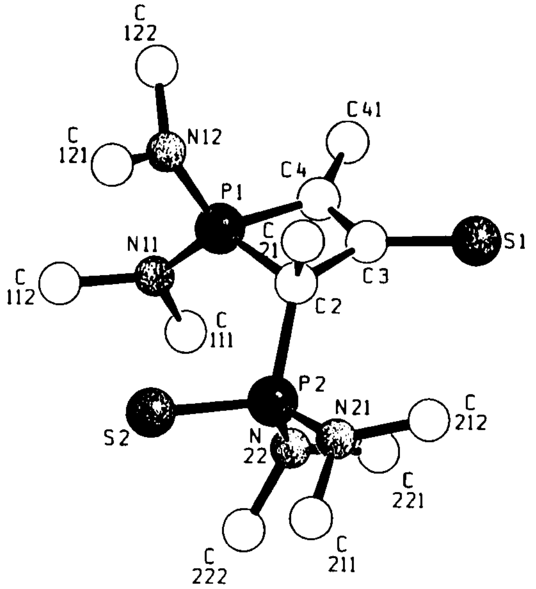

FIGURE 3 Molecular structure of one of the three crystallographically independent molecules of compound **7**.

IR, (as above): 1367 s, 1292 s, 1280 sh, 1219 vs, 1176 vs, 1072 m, 1060 m, 989 vs, 965 vs, 940 sh, 823 m, 771 s, 736 s, 641 s, 609 s, 525 m, 510 m, 472 s, 422 s, 402 w, 355 w, 306 w.

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