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The Crystal and Molecular Structures of 1,6-Diphosphatriptycene and 1,6-Diphosphatriptycene Dioxide

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1,6-Diphosphatriptycene ($C_{18}H_{12}P_2$) and 1,6-diphosphatriptycene dioxide ($C_{18}H_{12}P_2O_2$) crystallize isostructurally in the monoclinic space group $C2/c$, $Z=4$, with $a=15·068$ (5), $b=8·276$ (3), $c=13·305$ (3) Å, $\beta=120·26$ (2)°, and $a=15·411$ (17), $b=8·301$ (7), $c=13·827$ (9) Å, $\beta=122·24$ (5)° respectively. Intensities were collected on a four-circle diffractometer and the structures, which were solved by direct methods, refined to R 0·050 (1079 reflexions) and 0·055 (1197 reflexions). The molecules contain a space-group dyad axis in the plane of one of the benzene rings. Their thermal motion (with the exclusion of the P=O bond in the dioxide) is satisfactorily accounted for by application of the rigid-body hypothesis. Significant differences are observed between the two molecules in their bond lengths and angles at P. A mean P–C length (librationally corrected) of 1·845 (2) and C–P–C angle of 97·0 (2) in $C_{18}H_{12}P_2$ contrast with values of 1·827 (4) Å and 100·5 (1)° in $C_{18}H_{12}P_2O_2$.

Introduction

Electron diffraction (ED) studies of Me_3P (Bartell & Brockway, 1960) and Mc_3P=O (Wang, 1965) have demonstrated that the P–C length decreases and the C–P–C angle increases in these molecules on going from three- to four-coordination. A microwave (MW) investigation (Lide & Mann, 1958) provides corroboration of the molecular geometry of Me_3P. Values of 1·846(3) (ED) and 1·841(3) (MW) for P–C in Me_3P contrast with that of 1·813 Å (ED) in Me_3P=O. The increase in the C–P–C angle with increase in the coordination number is even more pronounced, from 98·6(3) (ED) and 99·1(2) (MW) in Me_3P to 106·0° (ED) in Me_3P=O. These observations are in accordance with an increase in the *s* character of the P–C bond on going from three- to four-coordination, accompanied by an increase in the C–P–C angle towards the tetrahedral angle, owing to the reduced degree of repulsion on the P–C bonds caused by the P=O bond, as opposed to the lone electron pair.

The caged 1,6-diphosphatriptycene (I) and its dioxide (II) (Weinberg & Whipple ,1971) provide model compounds for a further structural investigation of the nature of the bonding in such three- and four-coordinate P derivatives. For instance, the ^{31}P chemical shifts (upfield from an 85% H_3PO_4 external reference) for Ph_3P (8 p.p.m.) (Van Wazer, Callis, Shoolery & Jones, 1956), (I) (43 p.p.m.) and azaphosphatriptycene (80 p.p.m.) (Hellwinkel & Schenk, 1969) reflect the progressive distortion of the C–P–C angle required by the caged structures. In particular, it might be expected that the inability of the C–P–C angle in (II) to approach the tetrahedral angle required by sp^3 hybridization would lead to an increase in the *s* character of, and *ipso facto* a shortening in, the P=O bond compared with that in Me_3P=O.

Experimental

Crystals of (I) and (II), in the form of thin colourless plates, elongated along **c**, were obtained by slow cooling of saturated solutions in a methylene dichloride/ethanol mixture. Suitable crystals with approximate dimensions $0·8\times0·2\times0·05$ mm for (I) and $1·0\times0·3\times0·1$ mm for (II), mounted with **c** parallel to the goniometer axis, were used for all subsequent measurements. Systematic absences were observed for hkl, $h+k=2n+1$, and $h0l$, $l=2n+1$, indicating $C2/c$ or Cc as possible space groups for both compounds. Similarities in the cell parameters and in the intensity

Table 1. *Crystal data*

	(I)	(II)
Stoichiometry	$C_{18}H_{12}P_2$	$C_{18}H_{12}P_2O_2$
M	290·24	322·24
Space group	$C2/c$	$C2/c$
Z	4	4
a (Å)	15·068 (5)	15·411 (17)
b	8·276 (3)	8·301 (7)
c	13·305 (3)	13·827 (9)
β (°)	120·26 (2)	122·24 (5)
U (Å^3)	1433·1 (7)	1496·2 (19)
D_c (g cm^{-3})	1·35	1·43
(μMo $K\alpha$) (cm^{-1})	2·40	2·42

patterns on Weissenberg photographs suggested that (I) and (II) were isostructural; this was confirmed by the subsequent successful structure determination in $C2/c$. Accurate cell parameters were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex P2$_1$ four-circle diffractometer (Mo $K\alpha$ 0·71069 Å). These and other relevant crystal data are summarized in Table 1.

The intensities were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the θ–2θ mode ($3{\cdot}0\le 2\theta\le 50{\cdot}0°$) for one half of reciprocal space at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 19·53° min^{-1} (5000 c.p.s. and above). The angular 2θ range traversed was from 1·2° below the $K\alpha_1$ reflexion to 1·2° above the $K\alpha_2$ reflexion for (I), with respective values of 1·2° and 1·4° for (II). The net intensity of each reflexion (scaled to counts per minute) was assigned a standard deviation, based on the counting statistics, of $\sigma(I)=t(N_s+N_b)^{1/2}$, where t is the scan rate, N_s the gross count and N_b the total background count. Lorentz and polarization, but no absorption corrections, were applied. From the 2738 reflexions recorded for (I), those retained for use in the structure analysis had $F\ge 2{\cdot}5\sigma(F)$, $\sigma(F)$ being derived from $\sigma(I)$. Averaging of equivalencies yielded 1079 unique reflexions with $R_c=[\sum_1 w(F-G)^2/\sum_2 wG^2(m-1)]^{1/2}=0{\cdot}030$ where m is the number in a group of equivalent reflexions, G is the mean value of F for this group, $\sum_1$ is a summation over all reflexions and $\sum_2$ contains one contribution from each group of equivalent reflexions. For (II) 2884 reflexions were recorded, which, after data reduction, application of the rejection criterion $F\ge 2{\cdot}5\sigma(F)$ and subsequent averaging of equivalencies [$R_c=0{\cdot}083$], yielded 1197 unique reflexions.

Structure solution and refinement

The distribution of E values strongly suggested the space group $C2/c$ ($Z=4$) in which the molecules must contain a dyad axis. The structure of (II) was solved in $C2/c$ by a multisolution technique (Sheldrick, 1975) in which 2^{18} sign permutations were expanded by the $\sum_2$ formula. A permutation is rejected if its internal consistency falls at any stage below a preset value. Additionally, a test is applied to avoid the calculation of closely similar E maps. In this case five E maps were computed, of which the fourth best (in terms of $\sum_2$ consistency) revealed all atoms except C(8) and C(9) (Fig. 1). The solution and subsequent refinement of the structure were performed with *SHELX* written by G. M. Sheldrick.

The positional parameters of the remaining two C atoms were located from a difference synthesis. The structure was refined by full-matrix least squares, $\sum w\Delta^2$ being minimized; anisotropic temperature factors were introduced for all atoms. At this stage, a difference synthesis clearly revealed the positions of the H atoms, which were included, with their isotropic temperature factors, in the final cycles. The terminal value of $R_G=[\sum w\Delta^2/\sum wF_o^2]^{1/2}$ for (II) was 0·066, with $R_w=\sum w^{1/2}\Delta/\sum w^{1/2}F_o=0{\cdot}056$ and $R=0{\cdot}055$. The weights were given by $w=k/[\sigma^2(F_o)+gF_o^2]$ where k and g refined to 2·5155 and 0·000654 respectively. In the final cycle the largest observed shift/e.s.d. was $-0{\cdot}073$. A final difference synthesis displayed no peaks or troughs $>0{\cdot}46$ e Å^{-3}. 52 reflexions showed a deviation between F_o and F_c of more than $2\sigma(F_o)$. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed for the non-hydrogen atoms.

The refinement of (I) was initiated with the non-hydrogen atom parameters found for (II) (excluding the oxygen). The terminal values for the residuals, including refinement of H atom positional parameters

Table 2. *Atom positional parameters* ($\times 10^4$)

(I) 1,6-Diphosphatriptycene

	x	y	z
P	4657 (1)	2417 (1)	8473 (1)
C(1)	3836 (2)	1441 (3)	7052 (2)
C(2)	4131 (2)	1443 (3)	6209 (2)
C(3)	3542 (2)	660 (3)	5155 (2)
C(4)	2637 (2)	−144 (4)	4940 (3)
C(5)	2361 (2)	−166 (4)	5776 (3)
C(6)	2943 (2)	630 (3)	6822 (2)
C(7)	4851 (2)	4339 (3)	7920 (2)
C(8)	4709 (2)	5790 (3)	8331 (2)
C(9)	4859 (2)	7234 (3)	7912 (3)

(II) 1,6-Diphosphatriptycene dioxide

	x	y	z
P	4711 (1)	2363 (1)	8408 (1)
O	4443 (2)	2346 (4)	9263 (2)
C(1)	3827 (2)	1382 (3)	7042 (2)
C(2)	4090 (2)	1380 (3)	6217 (2)
C(3)	3475 (2)	595 (4)	5185 (3)
C(4)	2592 (3)	−204 (4)	4971 (3)
C(5)	2338 (3)	−214 (4)	5776 (3)
C(6)	2947 (2)	589 (4)	6824 (3)
C(7)	4867 (2)	4300 (3)	7910 (2)
C(8)	4737 (2)	5739 (4)	8321 (3)
C(9)	4872 (3)	7181 (4)	7905 (3)

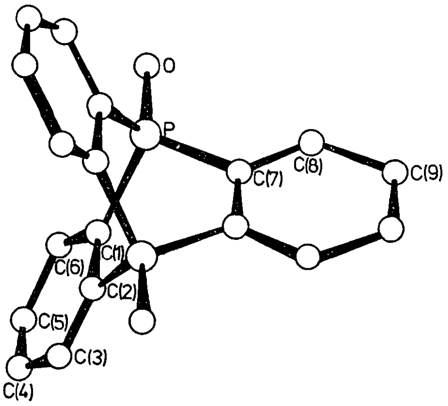

Fig. 1. Atom numbering in (II).

and isotropic temperature factors, were $R_G=0{\cdot}045$, $R_w=0{\cdot}044$, $R=0{\cdot}050$. In the weighting expression k and g refined to 2·391 and 0·000169 respectively. The largest observed shift/e.s.d. in the final cycle was −0·117. A final difference synthesis displayed no peaks or troughs >0·31 e Å^{-3}. 34 reflexions showed a deviation between F_o and F_c of more than $2\sigma(F_o)$. The final coordinates for (I) and (II) are listed in Table 2 and the anisotropic temperature factor components in Table 3. H atom positional parameters and isotropic temperature factors are given in Table 4. The full covariance matrix was implemented in the estimation of the bond lengths and selected bond angles presented in Tables 5 and 6.*

In view of their caged structures, the thermal motions in (I) and (II) should be well accounted for by the rigid-body model of Schomaker & Trueblood (1968). Accordingly, analyses were performed on the anisotropic temperature factor components with the program *RIGID* written by W.S.S. Good agreement was obtained between the observed and calculated U_{ij} values for both molecules (for (II) when the P=O bond was excluded with values for $R_G=[\sum\Delta^2/\sum U_o^2]^{1/2}$, $\Delta=U_o-U_c$, of 0·083 and 0·080 respectively). Root-

Table 3. *Anisotropic temperature factors* (Å^2 × 10^3)

The temperature factor takes the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}lhc^*a^*+2U_{12}hka^*b^*)\right]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(I) 1,6-Diphosphatriptycene						
P	48 (1)	38 (1)	41 (1)	1 (1)	24 (1)	3 (1)
C(1)	37 (1)	29 (1)	47 (2)	5 (1)	18 (1)	4 (1)
C(2)	41 (1)	27 (1)	40 (1)	2 (1)	15 (1)	1 (1)
C(3)	53 (2)	44 (2)	41 (2)	−3 (1)	15 (1)	0 (1)
C(4)	49 (2)	50 (2)	55 (2)	−9 (2)	7 (2)	−6 (2)
C(5)	42 (2)	55 (2)	74 (2)	1 (2)	16 (2)	−10 (2)
C(6)	40 (2)	49 (2)	57 (2)	9 (2)	22 (2)	3 (2)
C(7)	41 (2)	28 (1)	40 (2)	−2 (1)	12 (1)	3 (1)
C(8)	47 (2)	41 (2)	56 (2)	−11 (1)	16 (1)	7 (1)
C(9)	59 (2)	31 (2)	81 (3)	−12 (1)	12 (2)	5 (1)
(II) 1,6-Diphosphatriptycene dioxide						
P	38 (1)	34 (1)	37 (1)	2 (1)	21 (4)	4 (1)
O	82 (2)	81 (2)	73 (2)	5 (2)	50 (2)	10 (2)
C(1)	32 (2)	30 (1)	41 (2)	4 (1)	18 (1)	4 (1)
C(2)	34 (2)	27 (1)	39 (2)	0 (1)	17 (1)	1 (1)
C(3)	41 (2)	42 (2)	41 (2)	−3 (1)	15 (2)	0 (1)
C(4)	41 (2)	47 (2)	50 (2)	−10 (2)	7 (2)	−12 (2)
C(5)	35 (2)	53 (2)	66 (2)	6 (2)	15 (2)	−10 (2)
C(6)	36 (2)	47 (2)	55 (2)	8 (2)	22 (2)	1 (1)
C(7)	35 (2)	27 (1)	36 (2)	−2 (1)	12 (1)	3 (1)
C(8)	42 (2)	40 (2)	48 (2)	−7 (1)	13 (2)	8 (1)
C(9)	52 (2)	29 (2)	72 (3)	−10 (2)	10 (2)	5 (2)

Table 4. *Hydrogen atoms: positional parameters* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U
(I) 1,6-Diphosphatriptycene				
H(3)	3739 (17)	696 (29)	4523 (21)	39 (7)
H(4)	2226 (26)	−635 (39)	4198 (30)	82 (11)
H(5)	1783 (26)	−675 (38)	5633 (27)	75 (10)
H(6)	2715 (19)	671 (31)	7417 (22)	48 (8)
H(8)	4468 (20)	5863 (31)	8884 (24)	48 (8)
H(9)	4751 (26)	8123 (43)	8170 (29)	85 (11)
(II) 1,6-Diphosphatriptycene dioxide				
H(3)	3702 (24)	615 (37)	4551 (27)	43 (9)
H(4)	2215 (27)	−705 (40)	4313 (30)	51 (10)
H(5)	1784 (34)	−824 (50)	5701 (36)	82 (14)
H(6)	2751 (27)	573 (41)	7438 (29)	54 (11)
H(8)	4576 (30)	5861 (48)	8919 (34)	69 (13)
H(9)	4773 (29)	8171 (48)	8179 (32)	66 (11)

Table 5. *Bond lengths* (Å) *with librationally corrected values in square brackets*

	(I)	(II)
P——O		1·446 (3)
P——C(1)	1·844 (4) [1·849]	1·828 (3) [1·832]
P——C(2)′	1·838 (4) [1·844]	1·823 (3) [1·829]
P——C(7)	1·837 (4) [1·842]	1·815 (3) [1·820]
C(1)-C(2)	1·400 (5) [1·404]	1·400 (4) [1·404]
C(2)-C(3)	1·390 (5) [1·393]	1·384 (4) [1·387]
C(3)-C(4)	1·388 (6) [1·392]	1·396 (5) [1·400]
C(4)-C(5)	1·371 (6) [1·374]	1·363 (5) [1·367]
C(5)-C(6)	1·382 (6) [1·386]	1·405 (5) [1·408]
C(6)-C(1)	1·392 (5) [1·396]	1·387 (4) [1·391]
C(7)-C(8)	1·381 (5) [1·385]	1·383 (4) [1·387]
C(8)-C(9)	1·384 (6) [1·388]	1·391 (5) [1·395]
C(7)-C(7)′	1·398 (7) [1·402]	1·395 (6) [1·399]
C(9)-C(9)	1·362 (11) [1·365]	1·372 (8) [1·374]
C(3)-H(3)	1·04 (2)	1·10 (3)
C(4)-H(4)	0·95 (3)	0·88 (4)
C(5)-H(5)	0·90 (3)	0·95 (4)
C(6)-H(6)	1·01 (2)	1·05 (3)
C(8)-H(8)	0·97 (3)	0·99 (4)
C(9)-H(9)	0·86 (3)	0·95 (4)

Table 6. *Bond angles* (°)

	(I)	(II)
O——P——C(1)		117·2 (1)
O——P——C(2)′		116·8 (2)
O——P——C(7)		118·0 (1)
C(1)-P——C(2)′	96·9 (1)	100·3 (1)
C(1)-P——C(7)	97·4 (2)	100·6 (1)
C(2)′-P——C(7)	96·6 (1)	100·7 (1)
P——C(1)-C(2)	120·0 (3)	117·4 (2)
P——C(1)-C(6)	120·8 (3)	123·0 (3)
C(6)-C(1)-C(2)	119·1 (4)	119·5 (3)
C(1)-C(2)-C(3)	119·6 (4)	120·4 (3)
C(2)-C(3)-C(4)	120·5 (4)	119·6 (4)
C(3)-C(4)-C(5)	119·6 (4)	120·3 (4)
C(4)-C(5)-C(6)	120·8 (4)	120·8 (4)
C(5)-C(6)-C(1)	120·3 (4)	119·5 (4)
P——C(7)-C(7)′	120·0 (2)	117·7 (3)
P——C(7)-C(8)	120·5 (3)	122·4 (3)
C(7)′-C(7)-C(8)	119·5 (3)	120·3 (4)
C(7)-C(8)-C(9)	120·2 (4)	119·1 (4)
C(8)-C(9)-C(9)′	120·3 (4)	120·2 (4)
P′——C(2)-C(1)	119·8 (3)	117·2 (2)
P′——C(2)-C(3)	120·6 (3)	122·5 (3)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31034 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

mean-square discrepancies of 0·0033 and 0·0029 Å^2 were associated with these analyses. When the O atom was included in the analysis for (II), the value of R_G rose to 0·149 with an r.m.s. discrepancy of 0·0057 Å^2. The results of the rigid-body analysis are displayed in Table 7, where the tensors are as defined by Schomaker & Trueblood (1968), and have been used to apply the librational corrections to the bond lengths presented in Table 5. Figs. 1 and 2, which show the atom numbering in (II) and a projection of the contents of its unit cell perpendicular to [100], were drawn by the program *PANDORA* written by D. N. Lincoln and W.S.S.

Discussion

(I) and (II) crystallize isostructurally in the space group $C2/c$ with $Z=4$. A space-group dyad axis passes through the plane of one of the benzene rings in both cases. In addition, no significant distortions are observed for either molecule from D_{3h} symmetry, the highest which they may attain.

Table 7. *Rigid-body librational analysis*

Centre of mass (orthogonal coordinates*)

(I)	0·1663	0·2372	0·75
(II)	0·1410	0·2318	0·75

Tensors with respect to orthogonal axes and origin at the centre of mass with estimated standard deviations in parentheses.

(I)	T (Å × 10^{-4})	389 (11)	0	−27 (9)
			295 (9)	0
				351 (10)
(II)	T (Å × 10^{-4})	318 (9)	0	−33 (8)
			277 (8)	0
				325 (9)
(I)	L (rad × 10^{-4})	27 (2)	0	16 (1)
			29 (2)	0
				29 (2)
(II)	L (rad × 10^{-4})	25 (1)	0	15 (1)
			24 (2)	0
				32 (1)
(I)	S (Å . rad × 10^{-4})	−7 (2)	0	0 (2)
		0	8 (3)	0
		−6 (2)	0	0 (3)
(II)	S (Å . rad × 10^{-4})	−8 (2)	0	−4 (2)
		0	11 (2)	0
		−5 (2)	0	−3 (2)

Origin (orthogonal coordinates) which gives symmetric **S**:

(I)	0·1663	0·2499	0·75
(II)	0·1410	0·2337	0·75

Principal root-mean-square amplitudes and direction cosines.

(I)	T (Å†)			
	0·200	0·9651	0	0·2618
	0·172	0	1·0	0
	0·184	−0·2681	0	0·9651
(II)	T (Å†)			
	0·188	0·9846	0	−0·1747
	0·167	0	1·0	0
	0·169	0·1747	0	0·9846
(I)	L (rad)			
	0·035	0·7269	0	−0·6868
	0·054	0	1·0	0
	0·066	0·6868	0	0·7269
(II)	L (rad)			
	0·035	0·7779	0	−0·6283
	0·049	0	1·0	0
	0·066	0·6283	0	0·7779

* Referred to $a \sin\beta$, b, c.

† Reduced to keep U invariant.

A comparison between the results for (I) and (II) and those for Me_3P and $Me_3P{=}O$ is given in Table 8. The differences in the C–P–C angle and P–C lengths on passing from three-coordination in Me_3P to four-coordination in $Me_3P{=}O$ are paralleled, albeit less strikingly, in the results obtained for (I) and (II). In (I), the mean librationally corrected P–C length of 1·845(2) is not significantly different from those of 1·846(3) (ED) and 1·841(3) Å (MW) observed in the two studies of Me_3P. Similarly, the mean C–P–C angle is only 1·6° (ED) or 2·1° (MW), smaller than those in Me_3P. Inspection of the bond angles at C(1), C(2) and C(7) show that the C–P–C angle of 97·0(2)° can be assumed in (I) with very little distortion of these from 120·0°. However, the internal P–C–C angles, within the $P(CC)_3P$ cage, are significantly smaller [mean 119·9(1)°] than the external angles [mean 120·6(1)°]. Likewise, the lengths of 1·400(5) and 1·398(7) for C(1)–C(2) and C(7)–C(7)′, which lie

Table 8. *Structural data for* R_3P *and* $R_3P{=}O$ *compounds*

Distances in Å, angles in degrees.

Compound	P=O	P–C	C–P–C	Method
Me_3P	—	1·846 (3)	98·6 (3)	ED
Me_3P	—	1·841 (3)	99·1 (2)	MW
(I)	—	1·845 (2)*	97·0 (2)	XRD
$Me_3P{=}O$	1·479	1·813	106·0	ED
(II)	1·446 (3)	1·827 (4)*	100·5 (1)	XRD

* Librationally corrected mean values.

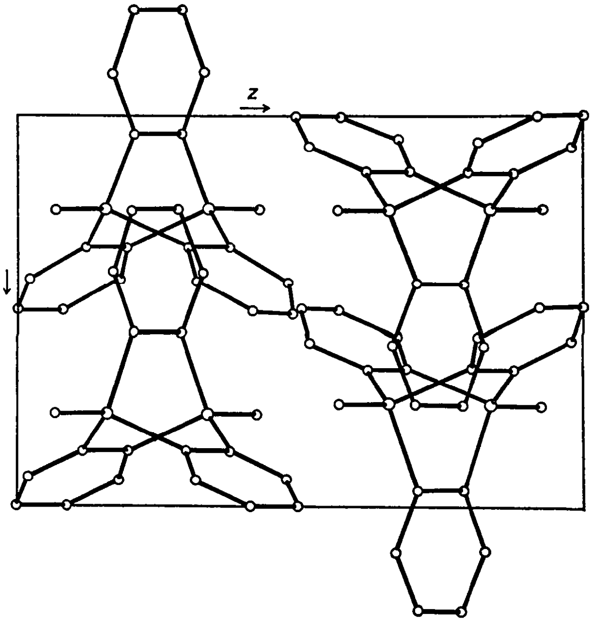

Fig. 2. Projection of the structure of (II) perpendicular to [100].

within the cage, are both considerably longer than those of 1·371(6) and 1·362(11) Å for the bonds opposite to them in the benzene rings.

The restriction, caused by the caged structure, on the ability of the C–P–C angle in (II) to approach the tetrahedral angle is dramatically underlined by a comparison of its mean value (100·5(1)°) with that of 106·0° in $Me_3P{=}O$. This limitation on the adoption of sp^3 hybridization at P leads to an increase in the s character of the P=O bond, as evidenced by its shortness in (II) (1·446(3) Å), compared to that of 1·479 Å in $Me_3P{=}O$. At the same time, the increase in the s character of the P–C bonds on going from (I) to (II) is significantly less than that observed in Me_3P and $Me_3P{=}O$. Thus the mean P–C length of 1·827(4) in (II) lies between that of 1·813 in $Me_3P{=}O$ and the range of values 1·841–1·846 Å observed for (I) and Me_3P. Considerable distortion is necessary in the trigonal angles at C(1), C(2) and C(7) in (II) to enable the achievement of the C–P–C angle of 100·5(1)°. The mean value for internal P–C–C angles, within the $P(CC)_3P$ cage, of 117·4(2)° is much smaller than that for the external angles of 122·6(2)°. As in (I), the C–C bonds within the $P(CC)_3P$ cage, C(1)–C(2) and C(7)–C(7)′, have lengths of 1·400(4) and 1·395(6) respectively, which are both considerably longer than those of 1·363(5) and 1·372(8) Å for the opposite bonds in the benzene rings, namely C(4)–C(5) and C(9)–C(9)′.

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Molekül- und Kristallstruktur des 1,2-Bis(methoxycarbonylamino)-3,5-dimethylpyrazolium-bromids

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1,2-Bis(methoxycarbonylamino)-3,5-dimethylpyrazolium bromide ($[C_9H_{15}N_4O_4]^+Br^-$) crystallizes in the monoclinic space group $P2_1/a$; $a = 14{\cdot}36_5$, $b = 12{\cdot}56_3$, $c = 8{\cdot}25_3$ Å, $\beta = 108{\cdot}3_2$°; $Z = 4$. The structure has been determined by the heavy-atom method using three-dimensional X-ray intensity data. The final R value is 4·7% for 2362 observed reflexions. All hydrogen atoms have been located and included in the refinement. The molecule consists of an almost planar pyrazolium ring substituted by two rotameric forms of urethane groups on different sides of the pyrazolium ring. The molecules are connected by H···Br bridges along a twofold screw axis parallel to **b**.

Einleitung

Durch Umsetzung von 3-Halogen-2,4-pentandionen (1) mit Alkoxy- (bzw. Alkyl-) carbonylhydrazinen (2) und anschliessender Behandlung des als Zwischenprodukt auftretenden Pyrazoliumsalzes (3) mit Alkalilauge oder wässriger Alkalihydrogencarbonatlösung erhält man nach dem angegebenem Reaktionsschema die neuartigen N-Imine des Pyrazols (5) (Sommer & Gieren, 1974).