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Structures of Three Diaryl-Substituted Triphenylphosphazines

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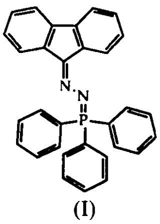
Abstract

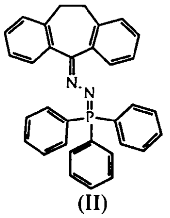
9-Fluorenone triphenylphosphazine (I), $C_{31}H_{23}N_2P$, $M_r = 454.51$, orthorhombic, $Pbca$, $a = 22.312\ (11)$, $b = 11.510\ (10)$, $c = 18.744\ (9)$ Å, $V = 4813\ (5)$ Å^3, $Z = 8$, $D_x = 1.25$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.31$ cm^{-1}, $F(000) = 1904$, $T = 294$ K, $R = 0.047$ for 2531 observed reflections. 10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one triphenylphosphazine (II), $C_{23}H_{27}N_2P$, $M_r = 482.57$, orthorhombic, $P2_12_12_1$, $a = 22.645\ (5)$, $b = 9.190\ (10)$, $c = 12.568\ (2)$ Å, $V = 2615\ (3)$ Å^3, $Z = 4$, $D_x = 1.23$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.24$ cm^{-1}, $F(000) = 1016$, $T = 294$ K, $R = 0.054$ for 2710 observed reflections. Benzophenone triphenylphosphazine (III), $C_{31}H_{25}N_2P$, $M_r = 456.53$, monoclinic, $P2_1/c$, $a = 13.730\ (5)$, $b = 17.205\ (10)$, $c = 10.914\ (4)$ Å, $\beta = 109.36\ (1)°$, $V = 2432\ (1)$ Å^3, $Z = 4$, $D_x = 1.25$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.30$ cm^{-1}, $F(000) = 960$, $T = 294$ K, $R = 0.058$ for 2541 observed reflections. The results confirm that the C—N—N—P phosphazine link is planar, implying strong conjugation, and that in (III) one of the C-phenyl substituents lies in a plane orthogonal to the C—N—N—P plane; both these findings accord with predictions made on the basis of kinetic studies of phosphazine formation.

Introduction

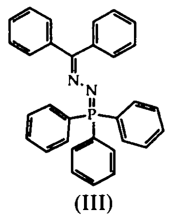
Phosphazines are prepared by the reaction of equimolar amounts of aliphatic diazo compounds with phosphines in what is generally regarded as a biphilic reaction, *i.e.* both reagents acting simultaneously as nucleophile and electrophile (Kirby & Warren, 1967). The reaction has attracted interest as a means of characterizing labile diazo compounds (Huisgen, 1955), and its biphilic nature has been explored by examining structural effects on the kinetics of reaction of diazoalkanes with triphenylphosphine and some substituted analogues (Goetz & Juds, 1964). Most recently frontier molecular orbital (FMO) theory has been used to interpret the reactivity of a group of α,α-diaryl-substituted diazoalkanes with triphenylphosphine (Bethell, Dunn, Khodaei & Newall, 1989), but this required assumptions to be made about the trajectory of approach of the reactants in order to select the interacting frontier orbitals. The trajectory, it was felt, should be reflected in the molecular structure of the product, but it was found that little was known about the structure of phosphazines, in particular about the extent of conjugation between the diazo-C and P atoms. A crystallographic investigation of compounds (I), (II) and (III) was therefore undertaken to answer this question. Information was also sought on the conformational situation of C-aryl groups in triphenylphosphazines. The rate of formation of (III) was found to be an order of magnitude faster than predicted by FMO theory and showed unexpected increases when substituents both with electron-donating and electron-withdrawing character were introduced into the diaryldiazoalkane precursor; this was thought to be the result of conformational changes in passing from the reactant to the transition state which would again be evident in the structure of (III).



(I)



(II)



(III)

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Experimental

Samples of (I), (II) and (III) were those previously described (Bethell, Dunn, Khodaei & Newall, 1989); suitable crystals were prepared by slow evaporation of acetonitrile solutions. Stoe Stadi-2 two-circle diffractometer, graphite-moderated Mo $K\alpha$ radiation. Cell parameters from least-squares analysis of 18–20 reflections measured in the range $8 < 2\theta < 25°$. Experimental data and refinement parameters are in Table 1. No absorption corrections. One standard reflection per layer, no significant variation. Structures solved by direct methods using *SHELX86* (Sheldrick, 1986) and refined (on *F*) using *SHELX76* (Sheldrick, 1976) including the atomic scattering factors therein. All non-H atoms were refined anisotropically. All H atoms in (I) located, but subsequently placed in calculated positions (C—H 1.08 Å) and allowed to ride on respective C atoms. The H atoms in (II) and (III) were not all located but placed in positions calculated as above. Isotropic *U* values for H atoms in (I) were allowed to refine individually, in (II) given a common fixed value (0.08 Å^2), and in (III) the common value was allowed to refine (final value 0.092 Å^2). In (II), many of the C atoms, especially C(4), C(5), C(10) and C(11), have anomalously large and anisotropic vibration parameters, indicating some form of disorder; it was not possible to locate H atoms on C(4) and C(5).

Discussion

Atomic coordinates and isotropic thermal parameters for (I)–(III) are in Table 2;* bond distances and angles are in Table 3. In Table 4, the deviations of the constituent atoms, P(1), N(1), N(2) and C(1), of the phosphazine linkage from the best plane are given, together with the angles made by this plane with the best planes through the two benzenoid moieties attached to C(1). Figs. 1, 2 and 3 show views of (I), (II) and (III) respectively, giving their numbering schemes.

The structure of the fluorenylidene moiety of (I) may usefully be compared with that of its precursor, 9-diazofluorene, and of 9-fluorenone (Tulip, Corfield & Ibers, 1978). The phosphazine shows the expected lengthening of the N—N distance from 1.126 (4) Å in the diazoalkane to 1.390 (4) Å, with a corresponding change from linearity in the C—N—N diazo group to a bond angle of 116.1 (2)°. In these respects the structure is very similar to that reported for planar and fully conjugated benzalazine, PhCH=N—N=CHPh (Sinha, 1970). The P—N—N angle of only 108.9 (2)° is more surprising. The remainder of the fluorenylidene group in (I) shows structural features, particularly bond lengths, that place it between 9-diazofluorene and 9-fluorenone, but with a rather closer correspondence to the latter in keeping with the lower electron density expected in the phosphazine compared with its precursor. The central P—N—N—C phosphazine linkage is very close to planarity as judged both from the torsion angle and the small deviations (<0.04 Å) of the constituent atoms from the average plane. Since this plane is almost coincident with the planes defined by the benzenoid rings of the fluorene unit, it would seem that π-conjugation extends through the whole of this part of the molecule. The phenyl groups attached to P show a propeller arrangement around an essentially tetrahedral central atom, although with some distortion of bond angles.

Table 1. *Experimental data and structure-refinement parameters*

		(I)	(II)	(III)
Crystal dimensions (mm)		0.13 × 0.40 × 0.45	0.40 × 0.31 × 0.2	0.45 × 0.35 × 0.20
Range of indices *h*		0 to 24	−16 to 16	0 to 16
k		0 to 12	0 to 10	0 to 20
l		0 to 20	0 to 29	−13 to 13
ω scans of width	*A*	1.0	1.5	1.0
($A + B \sin\mu/\tan\theta$)	*B*	0.6	0.6	0.6
2θ range (°)		$6 < 2\theta < 50$	$6 < 2\theta < 45$	$6 < 2\theta < 50$
Total No. of reflections		3608	3850	4563
No. of unique reflections		3475	3265	4217
$R_{\rm int}$		0.0021	0.0108	0.0056
No. of reflections used		2531 with $F > 4\sigma(F)$	2710 with $F > 4\sigma(F)$	2541 with $F > 6\sigma(F)$
No. of parameters		342	338	328
$\Delta\rho$ (min., max.) (e Å^{-3})		0.21, −0.27	0.27, −0.36	0.26, −0.37
Δ/σ (final)		< 0.06	< 0.2	< 0.02
R/wR		0.047/0.048	0.054/0.055	0.058/0.053
S		1.065	1.253	1.403
Weighting scheme,* *g*		5.4×10^{-4}	4.7×10^{-4}	9.3×10^{-5}

* $w = (\sigma^2F + gF^2)^{-1}$.

In (II) and (III) the geometry of the C—N—N—P group is very similar to that in (I), with the largest deviation from planarity in (II) (see the torsion angles in Table 3). The benzenoid rings in (II) are substantially and unsymmetrically inclined (by 56.4 and 27.2°) to the mean C—N—N—P plane, an arrangement that should allow a considerable degree of conjugation with the phosphazine group. In (III) the two C-phenyl substituents are rotated by 45.0 and 88.7° to the C—N—N—P plane and thus one of the rings cannot be conjugated at all with the phosphazine groups.

Taking the three compounds as a group, the bond lengths in the C—N—N—P moiety are all intermediate between those found for single and double bonds in appropriate models taken from the literature compilation of Allen, Kennard, Watson, Bramner, Orpen & Taylor (1987). This is taken as evidence that π-conjugation extends throughout the phosphazine grouping.

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54940 (43 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0116]

Table 2. *Fractional atomic coordinates and mean isotropic thermal parameters* (Å^2 × 10^3), *with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
9-Fluorenone triphenylphosphazine (I)				
P(1)	0.0499 (0)	0.2541 (1)	0.2045 (0)	36.6 (4)
N(1)	0.0934 (1)	0.3650 (2)	0.1926 (1)	46 (2)
N(2)	0.1147 (1)	0.3634 (2)	0.1229 (1)	44 (1)
C(1)	0.1545 (1)	0.4427 (2)	0.1068 (2)	39 (2)
C(2)	0.1836 (1)	0.5346 (2)	0.1488 (2)	39 (2)
C(3)	0.2263 (1)	0.5896 (3)	0.1043 (2)	43 (2)
C(4)	0.2245 (1)	0.5340 (3)	0.0337 (2)	44 (2)
C(5)	0.1816 (1)	0.4458 (2)	0.0253 (2)	42 (2)
C(6)	0.1709 (1)	0.3778 (3)	-0.0247 (2)	52 (2)
C(7)	0.2031 (2)	0.4007 (3)	-0.0865 (2)	62 (2)
C(8)	0.2449 (2)	0.4896 (3)	-0.0886 (2)	65 (2)
C(9)	0.2565 (2)	0.5569 (3)	-0.0289 (2)	59 (2)
C(10)	0.1767 (1)	0.5714 (3)	0.2191 (2)	45 (2)
C(11)	0.2126 (1)	0.6614 (3)	0.2441 (2)	51 (2)
C(12)	0.2557 (2)	0.7136 (3)	0.2004 (2)	54 (2)
C(13)	0.2622 (1)	0.6779 (3)	0.1299 (2)	53 (2)
C(101)	0.0624 (2)	0.3302 (3)	0.3431 (2)	52 (2)
C(102)	0.0491 (2)	0.3318 (3)	0.4155 (2)	66 (2)
C(103)	0.0051 (2)	0.2606 (3)	0.4423 (2)	61 (2)
C(104)	-0.0257 (2)	0.1878 (4)	0.3979 (2)	68 (2)
C(105)	0.0134 (2)	0.1864 (3)	0.3251 (2)	58 (2)
C(106)	0.0311 (1)	0.2582 (2)	0.2978 (1)	39 (2)
C(201)	0.0374 (2)	0.3612 (3)	0.1236 (2)	64 (2)
C(202)	-0.0915 (2)	0.3630 (4)	0.0835 (2)	88 (3)
C(203)	-0.1237 (2)	0.2625 (5)	0.0739 (2)	87 (3)
C(204)	-0.1051 (2)	0.1613 (4)	0.1023 (2)	74 (3)
C(205)	-0.0527 (1)	0.1571 (3)	0.1418 (2)	53 (2)
C(206)	-0.0185 (1)	0.2565 (3)	0.1526 (1)	42 (2)
C(301)	0.0870 (1)	0.0782 (3)	0.1146 (2)	51 (2)
C(302)	0.1151 (2)	-0.0253 (3)	0.0980 (2)	63 (2)
C(303)	0.1388 (2)	-0.0938 (3)	0.1513 (2)	69 (3)
C(304)	0.1353 (2)	-0.0577 (3)	0.2211 (2)	74 (3)
C(305)	0.1072 (2)	0.0457 (3)	0.2381 (2)	54 (2)
C(306)	0.0823 (1)	0.1148 (2)	0.1852 (2)	36 (2)
10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one triphenylphosphazine (II)				
P(1)	0.1251 (1)	0.3938 (1)	0.1888 (1)	50.4 (6)
N(1)	0.1784 (1)	0.2882 (4)	0.1544 (3)	61 (2)
N(2)	0.2278 (2)	0.3310 (5)	0.2132 (3)	66 (2)
C(1)	0.2788 (2)	0.2739 (6)	0.1826 (4)	69 (3)
C(2)	0.2862 (2)	0.1800 (6)	0.0867 (5)	74 (4)
C(3)	0.3115 (3)	0.0430 (8)	0.0957 (8)	118 (6)
C(4)	0.3312 (4)	-0.0037 (10)	0.2036 (9)	172 (8)
C(5)	0.3858 (4)	0.0746 (14)	0.2410 (7)	173 (9)
C(6)	0.3807 (3)	0.2412 (14)	0.2634 (6)	132 (7)
C(7)	0.3300 (2)	0.3266 (10)	0.2451 (5)	90 (5)
C(8)	0.3308 (3)	0.4715 (11)	0.2768 (4)	100 (5)
C(9)	0.3784 (4)	0.5356 (11)	0.3266 (5)	140 (7)
C(10)	0.4268 (5)	0.4484 (23)	0.3407 (10)	219 (17)
C(11)	0.4274 (7)	0.3080 (25)	0.3118 (11)	218 (19)
C(12)	0.2682 (2)	0.2279 (6)	-0.0126 (6)	79 (4)
C(13)	0.2760 (2)	0.1441 (8)	-0.1029 (6)	101 (5)
C(14)	0.3013 (3)	0.0098 (9)	-0.0952 (9)	129 (7)
C(15)	0.3187 (3)	-0.0443 (7)	0.0004 (9)	119 (6)
C(101)	0.1109 (2)	0.6976 (6)	0.2091 (4)	75 (3)
C(102)	0.1225 (3)	0.8400 (6)	0.1758 (5)	84 (4)
C(103)	0.1610 (2)	0.8655 (7)	0.0949 (5)	87 (4)
C(104)	0.1881 (3)	0.7533 (7)	0.0415 (5)	83 (4)
C(105)	0.1765 (2)	0.6125 (6)	0.0731 (4)	69 (3)
C(106)	0.1382 (2)	0.5822 (4)	0.1565 (3)	51 (3)
C(201)	0.0544 (2)	0.3140 (6)	0.3612 (4)	070 (3)
C(202)	0.0424 (3)	0.2990 (7)	0.4686 (5)	84 (4)
C(203)	0.0795 (3)	0.3627 (7)	0.5429 (4)	80 (4)
C(204)	0.1287 (3)	0.4372 (6)	0.5091 (4)	77 (4)
C(205)	0.1416 (2)	0.4501 (5)	0.4022 (4)	69 (3)
C(206)	0.1038 (2)	0.3881 (5)	0.3269 (4)	53 (2)
C(301)	0.0104 (2)	0.4157 (6)	0.1141 (4)	70 (3)
C(302)	-0.0378 (2)	0.3684 (9)	0.0547 (5)	86 (4)
C(303)	-0.0344 (3)	0.2480 (9)	-0.0069 (5)	95 (5)
C(304)	0.0178 (3)	0.1707 (7)	-0.0111 (6)	102 (5)
C(305)	0.0657 (2)	0.2141 (6)	0.0474 (4)	78 (3)
C(306)	0.0625 (2)	0.3357 (5)	0.1120 (4)	53 (3)
Benzophenone triphenylphosphazine (III)				
P(1)	0.8032 (1)	0.0107 (1)	0.2124 (1)	38.8 (4)
N(1)	0.7023 (2)	0.0250 (2)	0.0877 (3)	43 (1)
N(2)	0.6944 (2)	-0.0298 (2)	-0.0085 (3)	45 (1)
C(1)	0.6360 (3)	-0.0083 (2)	-0.1252 (3)	40 (2)
C(11)	0.6246 (3)	-0.1457 (3)	-0.2021 (4)	54 (2)
C(12)	0.6151 (3)	-0.2005 (3)	-0.2988 (4)	62 (2)
C(13)	0.6021 (3)	-0.1777 (3)	-0.4235 (4)	57 (2)
C(14)	0.5965 (3)	-0.0998 (2)	-0.4531 (4)	52 (2)
C(15)	0.6038 (3)	-0.0441 (2)	-0.3577 (3)	44 (2)
C(16)	0.6203 (3)	-0.0665 (2)	-0.2298 (3)	38 (2)
C(21)	0.6384 (3)	0.1283 (3)	-0.2018 (4)	52 (2)
C(22)	0.5931 (4)	0.1997 (3)	-0.2348 (4)	64 (2)
C(23)	0.4983 (4)	0.2151 (3)	-0.2204 (4)	64 (2)
C(24)	0.4496 (3)	0.1577 (3)	-0.1728 (4)	62 (2)
C(25)	0.4949 (3)	0.0859 (3)	-0.1422 (4)	51 (2)
C(26)	0.5893 (3)	0.0700 (2)	-0.1558 (3)	39 (2)
C(101)	0.6909 (3)	0.0760 (2)	0.3524 (4)	46 (2)
C(102)	0.6770 (3)	0.1204 (2)	0.4502 (4)	54 (2)
C(103)	0.7582 (3)	0.1641 (3)	0.5297 (4)	61 (2)
C(104)	0.8525 (3)	0.1629 (3)	0.5120 (4)	58 (2)
C(105)	0.8679 (3)	0.1179 (2)	0.4143 (4)	45 (2)
C(106)	0.7870 (3)	0.0740 (2)	0.3348 (3)	37 (2)
C(201)	0.8132 (3)	-0.1020 (3)	0.4009 (4)	59 (2)
C(202)	0.8258 (4)	-0.1768 (3)	0.4497 (4)	79 (3)
C(203)	0.8508 (3)	-0.2356 (3)	0.3810 (5)	70 (3)
C(204)	0.8651 (4)	-0.2197 (3)	0.2651 (5)	75 (3)
C(205)	0.8515 (3)	-0.1452 (3)	0.2140 (4)	64 (2)
C(206)	0.8254 (3)	-0.0853 (2)	0.2841 (3)	42 (2)
C(301)	1.0175 (3)	0.0096 (3)	0.2615 (4)	55 (2)
C(302)	1.1049 (4)	0.0317 (3)	0.2348 (5)	70 (2)
C(303)	1.0970 (4)	0.0810 (3)	0.1321 (5)	74 (2)
C(304)	1.0022 (3)	0.1082 (3)	0.0557 (4)	64 (2)
C(305)	0.9146 (3)	0.0868 (2)	0.0821 (4)	52 (2)
C(306)	0.9214 (3)	0.0364 (2)	0.1848 (3)	39 (2)

Table 3. *Selected bond lengths* (Å) *and angles* (°)

9-Fluorenone triphenylphosphazine (I)			
P(1)—N(1)	1.619 (3)	C(3)—C(13)	1.380 (4)
P(1)—C(106)	1.800 (3)	C(4)—C(5)	1.396 (4)
P(1)—C(206)	1.810 (3)	C(4)—C(9)	1.398 (5)
P(1)—C(306)	1.796 (3)	C(5)—C(6)	1.391 (4)
N(1)—N(2)	1.390 (4)	C(6)—C(7)	1.389 (5)
N(2)—C(1)	1.308 (4)	C(7)—C(8)	1.385 (5)
C(1)—C(2)	1.470 (4)	C(8)—C(9)	1.387 (5)
C(1)—C(5)	1.471 (4)	C(10)—C(11)	1.392 (4)
C(2)—C(3)	1.416 (4)	C(11)—C(12)	1.397 (5)
C(2)—C(10)	1.393 (4)	C(12)—C(13)	1.391 (5)
C(3)—C(4)	1.470 (4)		
N(1)—P(1)—C(106)	104.7 (1)	C(4)—C(3)—C(13)	130.5 (3)
N(1)—P(1)—C(206)	114.8 (1)	C(3)—C(4)—C(5)	108.4 (2)
N(1)—P(1)—C(306)	115.8 (1)	C(3)—C(4)—C(9)	131.2 (3)
C(106)—P(1)—C(206)	109.0 (1)	C(5)—C(4)—C(9)	120.4 (3)
C(106)—P(1)—C(306)	108.3 (1)	C(1)—C(5)—C(4)	108.7 (2)
C(206)—P(1)—C(306)	104.2 (1)	C(1)—C(5)—C(6)	130.7 (3)
P(1)—N(1)—N(2)	108.9 (2)	C(4)—C(5)—C(6)	120.7 (3)
N(1)—N(2)—C(1)	116.1 (2)	C(5)—C(6)—C(7)	118.6 (3)
N(2)—C(1)—C(2)	132.7 (3)	C(6)—C(7)—C(8)	120.9 (3)
N(2)—C(1)—C(5)	120.4 (2)	C(7)—C(8)—C(9)	121.0 (3)
C(2)—C(1)—C(5)	106.7 (2)	C(4)—C(9)—C(8)	118.5 (3)
C(1)—C(2)—C(3)	107.7 (2)	C(2)—C(10)—C(11)	118.7 (3)
C(1)—C(2)—C(10)	132.5 (3)	C(10)—C(11)—C(12)	121.3 (3)
C(3)—C(2)—C(10)	119.8 (3)	C(11)—C(12)—C(13)	120.1 (3)
C(2)—C(3)—C(4)	108.5 (2)	C(3)—C(13)—C(12)	119.2 (3)
C(2)—C(3)—C(13)	120.9 (3)		
P(1)—N(1)—N(2)—C(1)	-174.6 (2)	N(2)—C(1)—C(5)—C(6)	2.8 (5)
N(2)—C(1)—C(2)—C(10)	-3.2 (5)	C(13)—C(3)—C(4)—C(9)	-3.1 (6)
10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one triphenylphosphazine (II)			
P(1)—N(1)	1.607 (4)	C(4)—C(5)	1.505 (15)
P(1)—C(106)	1.803 (4)	C(5)—C(6)	1.561 (14)
P(1)—C(206)	1.803 (5)	C(6)—C(7)	1.409 (12)
P(1)—C(306)	1.796 (5)	C(6)—C(11)	1.366 (20)
N(1)—N(2)	1.398 (5)	C(7)—C(8)	1.390 (11)
N(2)—C(1)	1.324 (6)	C(8)—C(9)	1.379 (11)
C(1)—C(2)	1.492 (8)	C(9)—C(10)	1.370 (18)
C(1)—C(7)	1.483 (9)	C(10)—C(11)	1.341 (24)
C(2)—C(3)	1.388 (10)	C(12)—C(13)	1.383 (9)
C(2)—C(12)	1.385 (8)	C(13)—C(14)	1.364 (11)
C(3)—C(4)	1.490 (13)	C(14)—C(15)	1.59 (13)
C(3)—C(15)	1.450 (12)		
N(1)—P(1)—C(106)	113.3 (2)	C(3)—C(4)—C(5)	113.1 (8)
N(1)—P(1)—C(206)	116.3 (2)	C(4)—C(5)—C(6)	117.7 (8)
N(1)—P(1)—C(306)	105.6 (2)	C(5)—C(6)—C(7)	125.2 (8)

Table 3 (*cont.*)

C(106)—P(1)—C(206)	106.8 (2)	C(5)—C(6)—C(11)	117.6 (10)
C(106)—P(1)—C(306)	107.1 (2)	C(7)—C(6)—C(11)	117.0 (10)
C(206)—P(1)—C(306)	107.3 (2)	C(1)—C(7)—C(6)	122.8 (6)
P(1)—N(1)—N(2)	106.8 (3)	C(1)—C(7)—C(8)	118.3 (6)
N(1)—N(2)—C(1)	115.7 (4)	C(6)—C(7)—C(8)	118.5 (7)
N(2)—C(1)—C(2)	124.2 (5)	C(7)—C(8)—C(9)	123.3 (7)
N(2)—C(1)—C(7)	113.5 (5)	C(8)—C(9)—C(10)	115.8 (9)
C(2)—C(1)—C(7)	121.9 (5)	C(9)—C(10)—C(11)	122.4 (14)
C(1)—C(2)—C(3)	120.4 (5)	C(6)—C(11)—C(10)	123.1 (15)
C(1)—C(2)—C(12)	120.7 (5)	C(2)—C(12)—C(13)	121.7 (6)
C(3)—C(2)—C(12)	118.9 (6)	C(12)—C(13)—C(14)	120.0 (7)
C(2)—C(3)—C(4)	117.3 (7)	C(13)—C(14)—C(15)	121.0 (8)
C(2)—C(3)—C(15)	118.7 (7)	C(3)—C(15)—C(14)	119.7 (8)
C(4)—C(3)—C(15)	124.0 (8)		
P(1)—N(1)—N(2)—C(1)	−168.6 (4)	C(1)—C(2)—C(3)—C(4)	−0.9 (10)
N(1)—N(2)—C(1)—C(2)	5.2 (7)	C(3)—C(4)—C(5)—C(6)	66.7 (11)
N(1)—N(2)—C(1)—C(7)	178.0 (4)	C(11)—C(6)—C(7)—C(1)	172.9 (10)
Benzophenone triphenylphosphazine (III)			
P(1)—N(1)	1.606 (3)	N(1)—C(2)	1.388 (4)
P(1)—C(106)	1.794 (4)	N(2)—C(1)	1.314 (5)
P(1)—C(206)	1.811 (4)	C(1)—C(16)	1.479 (5)
P(1)—C(306)	1.800 (4)	C(1)—C(26)	1.483 (5)
C—C (benzene rings of =CPh$_2$ group)		1.37 (1)–1.40 (1)	
N(1)—P(1)—C(106)	104.6 (2)	P(1)—N(1)—N(2)	111.5 (2)
N(1)—P(1)—C(206)	118.7 (2)	N(1)—N(2)—C(1)	114.3 (3)
N(1)—P(1)—C(306)	113.1 (2)	N(2)—C(1)—C(16)	116.4 (3)
C(106)—P(1)—C(206)	106.1 (2)	N(2)—C(1)—C(26)	123.6 (3)
C(106)—P(1)—C(306)	108.5 (2)	C(16)—C(1)—C(26)	120.0 (3)
C(206)—P(1)—C(306)	105.3 (2)		
C—C—C (benzene rings of =CPh$_2$ group)		118.0 (1)–121.3 (1)	
P(1)—N(1)—N(2)—C(1)	−159.0 (3)	N(2)—C(1)—C(16)—C(15)	−150.1 (4)
N(1)—N(2)—C(1)—C(16)	−176.6 (3)	N(2)—C(1)—C(26)—C(21)	94.5 (5)
N(1)—N(2)—C(1)—C(26)	5.2 (5)	N(2)—C(1)—C(26)—C(25)	−87.1 (5)
N(2)—C(1)—C(16)—C(11)	28.1 (5)		

Table 4. *Deviations* (Å) *from planarity of the phosphazine linkage*

	(I)	(II)	(III)
P(1)	−0.026 (1)	−0.055 (1)	0.104 (1)
N(1)	0.022 (2)	0.044 (4)	−0.095 (3)
N(2)	0.038 (2)	0.083 (4)	−0.142 (3)
C(1)	−0.034 (3)	−0.072 (5)	0.133 (4)
Dihedral angle (°) to benzenoid rings attached to C(1)	7.6 (4), 5.6 (4)	56.4 (7), 27.2 (7)	45.0 (4), 88.7 (4)

While acknowledging caveats concerning the possible differences between molecular structures in the crystal and liquid phases, the results of this investigation clearly support the central assumption made in the earlier interpretation of the kinetics of phosphazine formation, namely, that the phosphazine linkage would be planar, with the corollary that it would be formed by way of a reaction trajectory in which the triphenylphosphine approaches the terminal N atoms of the diazoalkane in the nuclear plane of the diazo group and its two attached C—C bonds. Some support is also provided, through the disposition of the C-phenyl groups in (III), for the earlier suggestion of the importance of a homocon-

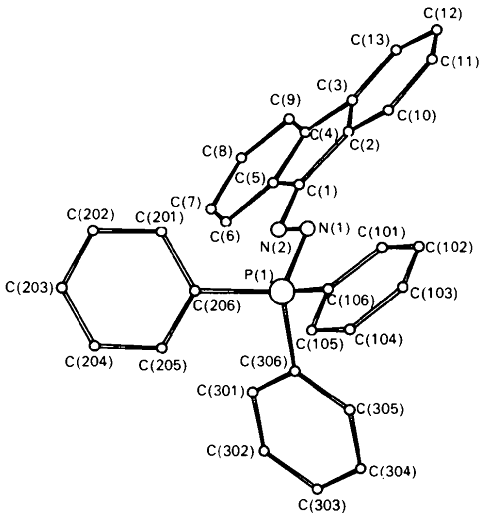

Fig. 1. *PLUTO* plot (Motherwell & Clegg, 1978) and numbering scheme for 9-fluorenone triphenylphosphazine (I) (H atoms omitted).

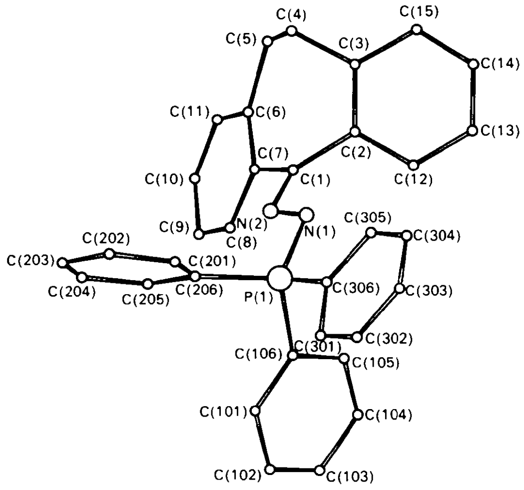

Fig. 2. *PLUTO* plot (Motherwell & Clegg, 1978) and numbering scheme for 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one triphenylphosphazine (II) (H atoms omitted).

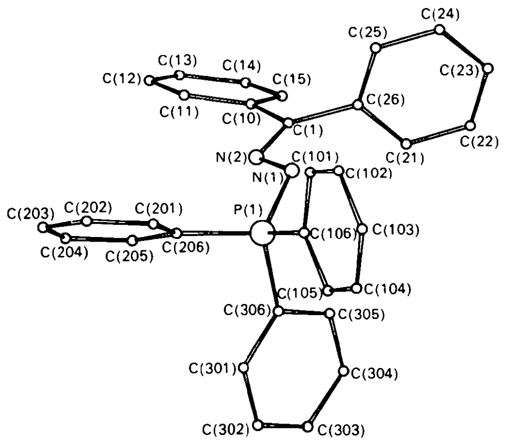

Fig. 3. *PLUTO* plot (Motherwell & Clegg, 1978) and numbering scheme for benzophenone triphenylphosphazine (III) (H atoms omitted).

jugative interaction between one aryl group in diazodiarylalkanes and the in-plane $\pi_{NN}{}^*$ orbital of the diazo group in determining the unusual pattern of reactivity with triphenylphosphine.

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Synthesis and Structure of New Bronchospasmolytic Agents. II

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Abstract

The crystal structures of four phenylethanolamines showing bronchospasmolytic activity have been determined at room temperature [293 (2) K]. Crystal data are as follows: 8-morpholinotricyclo[6.5.0.$0^{2,7}$]-trideca-2,4,6-trien-1-ol (2), $C_{17}H_{23}NO_2$, $M_r = 273.4$, monoclinic, $P2_1/n$, $a = 6.740$ (5), $b = 12.259$ (25), $c = 18.524$ (6) Å, $\beta = 90.01$ (4)°, $V = 1531$ (3) Å^3, $Z = 4$, $D_x = 1.186$ Mg m^{-3}, $\mu = 0.0719$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 592$, $R = 0.0372$ for 1556 observed reflections; 8-morpholinotricyclo-[6.5.0.$0^{2,7}$]trideca-2,4,6-triene-13-spiro-2′-(1′,3′-dioxan)-1-ol (3), $C_{20}H_{27}NO_4$, $M_r = 345.4$, triclinic, $P\bar{1}$, $a = 10.676$ (4), $b = 13.310$ (4), $c = 14.042$ (2) Å, $\alpha = 99.09$ (2), $\beta = 112.11$ (2), $\gamma = 95.03$ (3)°, $V = 1801.6$ (10) Å^3, $Z = 4$, $D_x = 1.274$ Mg m^{-3}, $\mu = 0.0823$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 744$, $R = 0.0389$ for 2871 observed reflections; 3-(2-methyl-1,3-dioxolan-2-yl)-8-morpholinotricyclo[6.5.0.$0^{2,7}$]trideca-2,4,6-trien-1-ol (4), $C_{21}H_{29}NO_4$, $M_r = 359.5$, monoclinic, $C2/c$, $a = 30.771$ (23), $b = 6.881$ (1), $c = 17.867$ (10) Å, $\beta = 99.10$ (8)°, $V = 3735$ (4) Å^3, $Z = 8$, $D_x = 1.278$ Mg m^{-3}, $\mu = 0.0819$ mm^{-1}, Mo $K\alpha_1$ radiation, $\lambda = 0.709300$ Å, $F(000) = 1552$, $R = 0.0392$ for 1575 observed reflections; 3-diethylamino-8-morpholinotricyclo[6.5.0.$0^{2,7}$]trideca-2,4,6-trien-1-ol (5), $C_{21}H_{32}N_2O_2$, $M_r = 344.5$, monoclinic, $P2_1/c$, $a = 10.017$ (1), $b = 10.823$ (2), $c = 18.143$ (3) Å, $\beta = 100.81$ (2)°, $V = 1932.0$ (5) Å^3, $Z = 4$, $D_x = 1.184$ Mg m^{-3}, $\mu = 0.5603$ mm^{-1}, Cu $K\alpha_1$ radiation, $\lambda = 1.5405620$ Å, $F(000) = 752$, $R = 0.0445$ for 2276 observed reflections. The *cis* configuration at the junction of the cyclobutene/cycloheptane rings is found for all the compounds, and indicates *syn* stereochemistry for the arynic condensation of the ketone enolate used for the preparation. The conformation of these molecules is discussed in connection with the central tricyclic system and the substituents on it. In all these molecules an intramolecular ring is present, formed by an O—H⋯N hydrogen-bonding interaction, between the alcoholic hydroxyl and the morpholine nitrogen, which determines the orientation of the morpholine substituent.

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