Discussion. The structure analysis confirms the stoichiometry of the title compound and the presence of two cyclometallated azobenzene ligands. The crystal structure consists of discrete molecular units; the closest intermolecular contact of 2·21 Å is between O(1) and H(25′) where H(25′) is related by the symmetry operation $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The coordination geometry about the Ru atom is defined by the two pairs of C and N donor atoms from the cyclometallated azobenzene ligands and two mutually *cis* carbonyl groups. N(1) is *trans* to the carbonyl CO(1) and N(3) is *trans* to the metallated C atom, C(14), so that the overall geometry of the complex is similar to that reported for the analogous Os compound (Dawoodi, Mays & Raithby, 1981). The five-membered Ru—C—C—N—N rings are essentially planar; the dihedral angle between the planes is *ca* 109°. The greatest deviations from ideal octahedral geometry about the Ru atom arise as a result of the restricted bite distance of the cyclometallated ligands [N(1)···C(14) 2·58 and N(3)···C(22) 2·60 Å, N(1)—Ru—C(14) 76·7 (3) and N(3)—Ru—C(22) 75·1 (3)°].

The Ru—N(3) [2·155 (7) Å] and Ru—C(22) [2·103 (8) Å] bonds *trans* to CO are longer than those *trans* to N or C(aryl) [Ru—N(1) 2·103 (6), Ru—C(14) 2·052 (7) Å] as expected from the greater *trans* effect of the CO ligands. Similarly, the Ru—CO(2) [1·930 (8) Å] bond is longer than Ru—CO(1) [1·879 (9) Å] as a result of the greater *trans* effect of C(aryl) *vs* N.

For complexes of this type, *i.e.* with *cis* monodentate ligands and two cyclometallated groups, three different arrangements of the cyclometallated donor atoms are possible. The title compound, and the Os analogue, adopt a conformation similar to that found for $\mathrm{Ru\{(C_6H_4O)P(OC_6H_5)_2\}_2}(L)_2$ with $L = \mathrm{P(OC_6H_5)_3}$ (Garbauskas, Kasper & Lewis, 1984) and $L = \mathrm{CO}$ (Bruce, Snow & Tiekink, 1986). An alternative conformation, with the N atoms *trans* and the metallated C atoms *cis* to each other, has been reported for $\mathrm{Rh\{C_6H_4N{=}NC_6H_5\}_2(O_2CCH_3)}$ (Craik, Knox, Pauson, Hoare & Mills, 1971). The third possible isomer has been found in $\mathrm{Ru(CO)_2(bq)_2}$ (bq = benzo[*h*]quinolin-10-yl), in which both of the N atoms are *trans* to carbonyl groups (Patrick, White, Bruce, Beatson, Black, Deacon & Thomas, 1983).

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References

BRUCE, M. I., SNOW, M. R. & TIEKINK, E. R. T. (1986). *J. Organomet. Chem.* **311**, 217–223.

CLEGG, W., SHELDRICK, G. M., STALKE, D., BHADURI, S. & GOPALKRISHNAN, K. S. (1984). *Acta Cryst.* C**40**, 927–929.

CRAIK, A. R. M., KNOX, G. R., PAUSON, P. L., HOARE, R. J. & MILLS, O. S. (1971). *J. Chem. Soc. Chem. Commun.* pp. 168–169.

DAWOODI, Z., MAYS, M. J. & RAITHBY, P. R. (1981). *Acta Cryst.* B**37**, 252–254.

GARBAUSKAS, M. F., KASPER, J. S. & LEWIS, L. N. (1984). *J. Organomet. Chem.* **276**, 241–248.

HAMILTON, W. C. & IBERS, J. A. (1974). Editors. *International Tables for X-ray Crystallography*, Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

PATRICK, J. M., WHITE, A. H., BRUCE, M. I., BEATSON, M. J., BLACK, D. ST C., DEACON, G. B. & THOMAS, N. C. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2121–2123.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1987). C**43**, 245–249

Structures of Five *N,N′*-Bis[(dialkoxyphosphinoyl)methyl]-1,4-benzenediamines

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Abstract. *N,N′*-Bis[(diethoxyphosphinoyl)methyl]-1,4-benzenediamine, $C_{16}H_{30}N_2O_6P_2$ (I), $M_r = 408{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}654\,(1)$, $b = 8{\cdot}732\,(1)$, $c = 11{\cdot}092\,(1)$ Å, $\alpha = 75{\cdot}95\,(1)$, $\beta = 86{\cdot}89\,(1)$, $\gamma = 84{\cdot}11\,(1)°$, $V = 528{\cdot}2\,(4)$ Å^3, $Z = 1$, $D_x = 1{\cdot}28$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}24$ mm^{-1},

0108-2701/87/020245-05$01.50

$F(000) = 218$, room temperature. Final $R = 0{\cdot}0497$ for 1372 observed reflections. *N,N'*-Bis[(di-*β*-chloroethoxyphosphinoyl)methyl]-1,4-benzenediamine, $C_{16}H_{26}Cl_4N_2O_6P_2$ (II), $M_r = 546{\cdot}2$, monoclinic, $P2_1/c$, $a = 14{\cdot}439$ (2), $b = 5{\cdot}641$ (3), $c = 15{\cdot}034$ (3) Å, $\beta = 102{\cdot}06$ (2)°, $V = 1197{\cdot}5$ (5) Å^3, $Z = 2$, $D_x = 1{\cdot}51$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}662$ mm^{-1}, $F(000) = 564$, room temperature. Final $R = 0{\cdot}0518$ for 1541 observed reflections. *N,N'*-Dibenzoyl-*N,N'*-bis[(diethoxyphosphinoyl)methyl]-1,4-benzenediamine, $C_{30}H_{38}N_2O_8P_2$ (III), $M_r = 616{\cdot}6$, orthorhombic, *Pbca*, $a = 8{\cdot}963$ (3), $b = 15{\cdot}543$ (7), $c = 23{\cdot}560$ (8) Å, $V = 3282{\cdot}2$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}187$ mm^{-1}, $F(000) = 1304$, room temperature. Final $R = 0{\cdot}0581$ for 1185 observed reflections. *N,N'*-Bis[(dimethoxyphosphinoyl)phenylmethyl]-1,4-benzenediamine, $C_{24}H_{30}N_2O_6P_2$ (IV), $M_r = 504{\cdot}5$, triclinic, $P\bar{1}$, $a = 8{\cdot}621$ (2), $b = 8{\cdot}949$ (4), $c = 9{\cdot}546$ (2) Å, $\alpha = 81{\cdot}14$ (4), $\beta = 65{\cdot}14$ (2), $\gamma = 69{\cdot}89$ (3)°, $V = 627{\cdot}4$ (3) Å^3, $Z = 1$, $D_x = 1{\cdot}33$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}220$ mm^{-1}, $F(000) = 266$, room temperature. Final $R = 0{\cdot}0453$ for 1673 observed reflections. *N,N'*-Bis[(diethoxyphosphinoyl)phenylmethyl]-1,4-benzenediamine, $C_{28}H_{38}N_2O_6P_2$ (V), $M_r = 560{\cdot}6$, triclinic, $P\bar{1}$, $a = 8{\cdot}882$ (1), $b = 9{\cdot}112$ (1), $c = 10{\cdot}322$ (2) Å, $\alpha = 99{\cdot}77$ (1), $\beta = 96{\cdot}36$ (1), $\gamma = 113{\cdot}23$ (1)°, $V = 741{\cdot}8$ (5) Å^3, $Z = 1$, $D_x = 1{\cdot}25$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1{\cdot}670$ mm^{-1}, $F(000) = 298$, room temperature. Final $R = 0{\cdot}0649$ for 1456 observed reflections. Owing to steric hindrance and the presence of the bulky phosphonic ester group, the phenyl rings in (III), (IV) and (V) are rotated with respect to one another by 67·3 (2)° (III), 85·7 (2)° (IV) and 93·0 (2)° (V). The C(phenyl)—N4—C5—C(phenyl) torsion angles are 28·7 (3)° (III), 64·3 (3)° (IV), and 72·6 (3)° (V). Structures (I), (II), (IV) and (V) are consolidated by the same type of intermolecular hydrogen bonds between the amino and phosphonic groups [P=O···H—N] with O···H distances 2·07 (5) Å (I), 2·25 (9) Å (II), 2·31 (3) Å (IV) and 2·10 (7) Å (V).

Introduction. In order to enhance the fire resistance of polyamides, new phosphorus-containing diamines of general type *N,N'*-bis[(dialkoxyphosphinoyl)methyl]-1,4-benzenediamine and polyamides and copolyamides derived from them were synthesized (Kallitsis & Tsolis, 1986; Kallitsis, 1986). The chloroethyl compound (II) was prepared because of the well known fire resistance of chlorinated polyamides and to examine the synergism between phosphorus and chlorine. *N,N'*-Dibenzoyl derivatives, *e.g.* (III), serve as model compounds of the polyamides. Attempts to polymerize the *N,N'*-bis[(dialkoxyphosphinoyl)phenylmethyl]-1,4-benzenediamines (IV and V) failed. The importance of the conformation in the enhancement of the chain length of the polymers is of interest and we decided to undertake the crystal structure determinations of the title compounds.

Experimental. (I). Crystal 0·35 × 0·26 × 0·74 mm, Siemens Kristaloflex 805 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters determined from 15 high-angle reflections, $\omega/2\theta$ scan technique up to $2\theta = 50°$, $-6 \le h \le 6$, $-9 \le k \le 10$, $0 \le l \le 13$, one standard reflection monitored every 50 reflections showed no significant deterioration in intensity. 1858 unique measured reflections of which 1372 observed with $I > 2{\cdot}5\sigma(I)$. $R = 0{\cdot}0497$ for 1372 unique reflections, $wR = 0{\cdot}0535$, $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F) + 0{\cdot}00032F^2]$, max. Δ/σ (for non-H atoms) = 0·46; max. and min. electron densities in final difference map 0·23 and −0·26 e Å^{-3}. All non-H atoms refined with anisotropic thermal parameters, all H atoms were placed in geometrically calculated positions, riding model, except H2, H3 and H4 which were located by a difference Fourier synthesis and refined isotropically.

(II). 0·32 × 0·25 × 0·65 mm, Enraf–Nonius CAD-4 (Mo $K\alpha$), 15 reflections, $2\theta < 24°$ for lattice parameters, $\omega/2\theta$ scan, $2\theta \le 50°$, $-17 \le h \le 16$, $0 \le k \le 6$, $0 \le l \le 17$, one standard reflection monitored every 50 without significant deviation. 2106 unique measured reflections, 1541 observed with $I > 2{\cdot}5\sigma(I)$, $R = 0{\cdot}0518$, $wR = 0{\cdot}063$, $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F) + 0{\cdot}00167F^2]$, max. Δ/σ (for non-H atoms) = 0·48, max. and min. electron densities in final difference map 0·67 and −0·37 e Å^{-3}. H atoms calculated except H2, H3 and H4 which were located and refined with isotropic temperature factors. All non-H atoms refined anisotropically.

(III). 0·40 × 0·32 × 0·68 mm, Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$), 15 reflections, $2\theta < 27°$, $\omega/2\theta$ scan, $2\theta \le 47°$, $0 \le h \le 9$, $0 \le k \le 16$, $0 \le l \le 26$, one standard reflection monitored every 50 showed only random deviation from its mean intensity. 2429 unique measured reflections, 1185 observed with $I > 2{\cdot}5\sigma(I)$, $R = 0{\cdot}0581$, $wR = 0{\cdot}06$, $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F) + 0{\cdot}00088F^2]$, max. Δ/σ (for non-H atoms) = 0·038, max. and min. electron densities in final difference map 0·30 and −0·24 e Å^{-3}. H atoms included in calculations with an overall isotropic temperature factor in idealized positions, except H2 and H3 which were found from ΔF synthesis and refined isotropically. Anisotropic thermal parameters for the non-H atoms.

(IV). 0·30 × 0·42 × 0·82 mm, Enraf–Nonius CAD-4 (Mo $K\alpha$), 25 reflections, $2\theta \le 26°$, $\omega/2\theta$ scan, $2\theta \le 47°$, $-8 \le h \le 9$, $-9 \le k \le 9$, $0 \le l \le 10$, one standard reflection monitored every 50 without significant deviation. 1842 unique measured reflections, 1673 observed with $I > 2{\cdot}5\sigma(I)$, $R = 0{\cdot}0453$, $wR = 0{\cdot}0609$, $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F) +$

$0{\cdot}00332F^2$], max. Δ/σ (for non-H atoms) = 0·66, max. and min. electron densities in final difference map 0·32 and −0·39 e Å^{-3}. H atoms calculated except H2, H3, H4 which were located and refined isotropically. All non-H atoms refined with anisotropic temperature factors.

(V). 0·38 × 0·34 × 0·87 mm, Siemens Kristaloflex 805 (Cu $K\alpha$), 15 high-angle reflections, $\omega/2\theta$ scan, $2\theta \leq 100°$, $-8 \leq h \leq 8$, $-9 \leq k \leq 8$, $0 \leq l \leq 10$, 1522 unique measured reflections, 1456 observed with $I > 2{\cdot}5\sigma(I)$, $R = 0{\cdot}0649$, $wR = 0{\cdot}0841$, $\sum w(\Delta F)^2$ minimized, $w = 1/[\sigma^2(F) + 0{\cdot}00066F^2]$, max. Δ/σ (for non-H atoms) = 0·62, max. and min. electron densities in final difference map 0·40 and −0·45 e Å^{-3}. H atoms calculated except H2, H3, H4 which were located and refined with isotropic thermal parameters. Non-H atoms refined anisotropically.

Table 1. *Fractional atomic coordinates* (× 10^4) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2 × 10^2)

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I)				
C1	−812 (5)	752 (4)	5956 (3)	357
C2	−2230 (5)	788 (4)	4969 (3)	379
C3	1456 (5)	−43 (4)	5966 (3)	399
N4	−1681 (5)	1574 (4)	6855 (3)	496
C5	−684 (6)	1245 (4)	8078 (3)	460
P6	1333 (2)	2681 (1)	8149 (1)	414
O7	3433 (4)	2703 (3)	7317 (2)	587
O8	1845 (5)	2233 (3)	9570 (2)	610
C9	3467 (9)	3154 (6)	10056 (4)	738
C10	4837 (8)	2078 (6)	11047 (4)	809
O11	−184 (4)	4321 (3)	7970 (2)	542
C12	−121 (8)	5563 (6)	6831 (5)	839
C13	−2376 (8)	5920 (6)	6243 (4)	831
H2	−3795 (76)	1396 (54)	4975 (38)	915
H3	2424 (81)	−59 (56)	6605 (40)	915
H4	−3172 (85)	1899 (57)	6818 (40)	915
(II)				
C1	5570 (4)	−823 (10)	9404 (4)	227
C2	5469 (4)	−2139 (11)	10159 (4)	246
C3	5095 (4)	1326 (11)	9257 (4)	243
N4	6163 (4)	−1668 (11)	8843 (4)	306
C5	6091 (5)	−827 (11)	7917 (4)	268
P6	6919 (1)	1497 (3)	7859 (1)	238
O7	6721 (4)	3823 (8)	8203 (3)	356
O8	6955 (3)	1418 (8)	6817 (3)	301
C9	7501 (5)	3215 (13)	6444 (5)	365
C10	7591 (5)	2458 (14)	5516 (5)	372
Cl11	8276 (2)	−128 (5)	5551 (2)	585
O12	7931 (3)	644 (8)	8399 (3)	310
C13	8366 (5)	−1540 (13)	8194 (5)	361
C14	9339 (5)	−1661 (16)	8754 (5)	436
Cl15	10048 (2)	653 (5)	8485 (2)	672
H2	5879 (49)	−3532 (130)	10333 (47)	456
H3	5185 (47)	2192 (142)	8816 (48)	456
H4	6541 (51)	−2926 (146)	9016 (49)	456
(III)				
C1	1239 (6)	228 (4)	9684 (2)	273
C2	−183 (6)	387 (4)	9477 (2)	306
C3	1421 (7)	−168 (4)	10206 (2)	298
N4	2522 (5)	448 (3)	9345 (2)	297
C5	3787 (7)	838 (4)	9566 (3)	310
O6	4986 (5)	767 (3)	9327 (2)	431
C7	3607 (7)	1402 (4)	10073 (2)	294
C8	2380 (8)	1917 (4)	10155 (3)	414
C9	2344 (9)	2486 (5)	10610 (3)	500
C10	3522 (9)	2524 (5)	10983 (3)	501
C11	4750 (8)	2019 (5)	10904 (3)	469
C12	4810 (7)	1452 (4)	10441 (3)	398
C13	2659 (7)	30 (4)	8787 (2)	361
P14	2206 (2)	736 (1)	8202 (1)	422
O15	765 (5)	1157 (4)	8225 (2)	604
O16	2443 (6)	89 (4)	7714 (2)	682
C17	2110 (11)	303 (7)	7125 (3)	811
C18	2224 (14)	−400 (8)	6783 (3)	1132
O19	3580 (6)	1348 (4)	8157 (2)	703
C(20)	3613 (17)	2167 (10)	8094 (9)	1772
C21	4383 (24)	2754 (10)	8038 (8)	1796
H2	−354 (52)	659 (32)	9118 (21)	286
H3	2477 (56)	−239 (29)	10345 (20)	231

Table 1 (*cont.*)

	x	y	z	B_{eq}
(IV)				
C1	5967 (3)	3572 (3)	5541 (3)	269
C2	6082 (4)	3715 (3)	4036 (3)	301
C3	4856 (3)	4901 (3)	6505 (3)	307
N4	6892 (3)	2113 (3)	6054 (3)	316
C5	7017 (3)	2041 (3)	7529 (3)	292
C6	8074 (3)	3043 (3)	7663 (3)	294
C7	7439 (4)	3893 (3)	9008 (3)	353
C8	8372 (4)	4840 (3)	9123 (4)	423
C9	9938 (4)	4936 (3)	7895 (4)	422
C10	10592 (4)	4068 (4)	6582 (4)	444
C11	9657 (4)	3116 (4)	6454 (3)	393
P12	7922 (1)	−42 (1)	7980 (1)	307
O13	9659 (3)	−885 (2)	6811 (2)	431
O14	6403 (3)	−823 (2)	8382 (2)	414
C15	6258 (5)	−1602 (4)	7242 (4)	507
O16	7858 (3)	119 (2)	9614 (2)	388
C17	8346 (6)	−1212 (4)	10550 (4)	552
H2	6869 (50)	2823 (45)	3383 (41)	631
H3	4556 (46)	4963 (41)	7679 (41)	631
H4	7815 (51)	1695 (46)	5431 (43)	631
(V)				
C1	8504 (5)	8547 (5)	9520 (4)	389
C2	9641 (6)	9142 (6)	8693 (5)	462
C3	8908 (5)	9420 (5)	10821 (5)	430
N4	6976 (4)	7152 (4)	9073 (4)	444
C5	6617 (5)	6066 (5)	7760 (4)	425
C6	7555 (5)	4993 (5)	7618 (4)	433
C7	8128 (6)	4705 (6)	6453 (5)	562
C8	8972 (7)	3685 (7)	6309 (7)	700
C9	9278 (7)	3024 (7)	7364 (7)	706
C10	8700 (8)	3290 (7)	8497 (6)	722
C11	7861 (7)	4277 (6)	8654 (5)	631
P12	4355 (1)	4871 (1)	7400 (1)	444
O13	3753 (4)	4067 (4)	8461 (3)	580
O14	3607 (4)	6048 (4)	7019 (3)	573
C15	3192 (8)	7141 (8)	8034 (7)	793
C16	4121 (14)	8859 (10)	8000 (11)	1269
O17	3942 (4)	3696 (4)	5970 (3)	535
C18	3736 (11)	2018 (8)	5813 (8)	980
C19	2488 (21)	926 (12)	5174 (13)	2120
H2	9506 (96)	8662 (88)	7915 (76)	1133
H3	8177 (95)	8716 (84)	11345 (70)	1133
H4	6610 (93)	6725 (93)	9751 (77)	1133

Table 2. *Selected bond lengths* (Å) *and bond angles* (°) [C(*P*) *denotes* C5, *except in* (III) *where it denotes* C13]

	(I)	(II)	(III)	(IV)	(V)
N4–C1	1·405 (4)	1·405 (7)	1·442 (7)	1·413 (3)	1·404 (5)
N4–C(*P*)	1·449 (4)	1·454 (8)	1·471 (7)	1·446 (3)	1·455 (5)
N4–H4	0·862 (46)	0·900 (81)	–	0·770 (32)	0·889 (70)
P=O	1·462 (2)	1·461 (4)	1·448 (5)	1·461 (2)	1·454 (3)
C1–N4–C(*P*)	122·3 (3)	122·2 (6)	117·3 (5)	119·3 (2)	120·5 (3)
C1–N4–H4	115·3 (31)	120·2 (47)	–	113·1 (26)	111·1 (49)
C(*P*)–N4–H4	115·5 (29)	116·9 (47)	–	110·6 (25)	119·3 (48)
N4–C(*P*)–P	110·7 (2)	111·8 (5)	113·2 (4)	107·7 (1)	104·7 (3)

Hydrogen-bonding distances			Equivalent position of H(4)N
(I)	P=O7···H4–N	2·069 (48)	$1+x, y, z$
(II)	P=O7···H4–N	2·249 (86)	$x, 1+y, z$
(IV)	P=O13···H4–N	2·307 (34)	$2-x, -y, 1-z$
(V)	P=O13···H4–N	2·104 (73)	$1-x, 1-y, 2-z$

Intensities corrected for Lp, secondary extinction and absorption corrections not used, atomic scattering factors from *SHELX76*. All structures solved by direct methods. Computer programs used for all structures: *MULTAN*11/84 (Main, Germain & Woolfson, 1984), *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Some of the terminal atoms of the ethoxyphosphinoyl groups may be affected by disorder, as shown by high thermal parameters (see Table 1).

Discussion. Final atomic parameters are given in Table 1* with selected bond lengths and angles in Table 2. Views of the five molecules with numbering are depicted in Figs. 1 and 2. The bond lengths and angles are in good agreement with those found for other analogous compounds (Harkema & Gaymans, 1977; Adams, Fratini & Wiff, 1978; Calabrese & Gardner, 1985).

In compounds (III), (IV) and (V) the angles between the phenyl groups are 67·35 (20), 85·69 (22) and 93·00 (23)° respectively. This twisting is due to steric hindrance and to the presence of the bulky phosphonic ester chain. The orientation of the phenyl groups has a significant influence on the crystal packing. The chain linking the two phenyl rings exists in a bent conformation defined by the torsion angle C(phenyl)—N4—C5—C(phenyl). The value of this torsion angle is −28·74 (30)° (III), −64·26 (31)° (IV), and 72·63 (33)° (V). Intermolecular hydrogen bonds exist for all structures except (III). These stabilize the crystal structures. In every case the same groupings are involved, *i.e.* $P{=}O\cdots H{-}N$. (see Table 2).

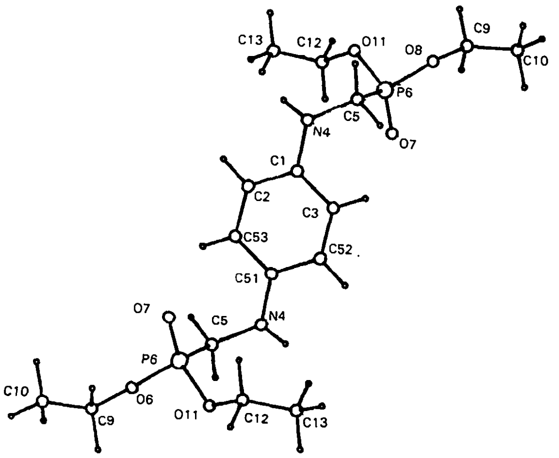

Fig. 1. Perspective view of compound (I).

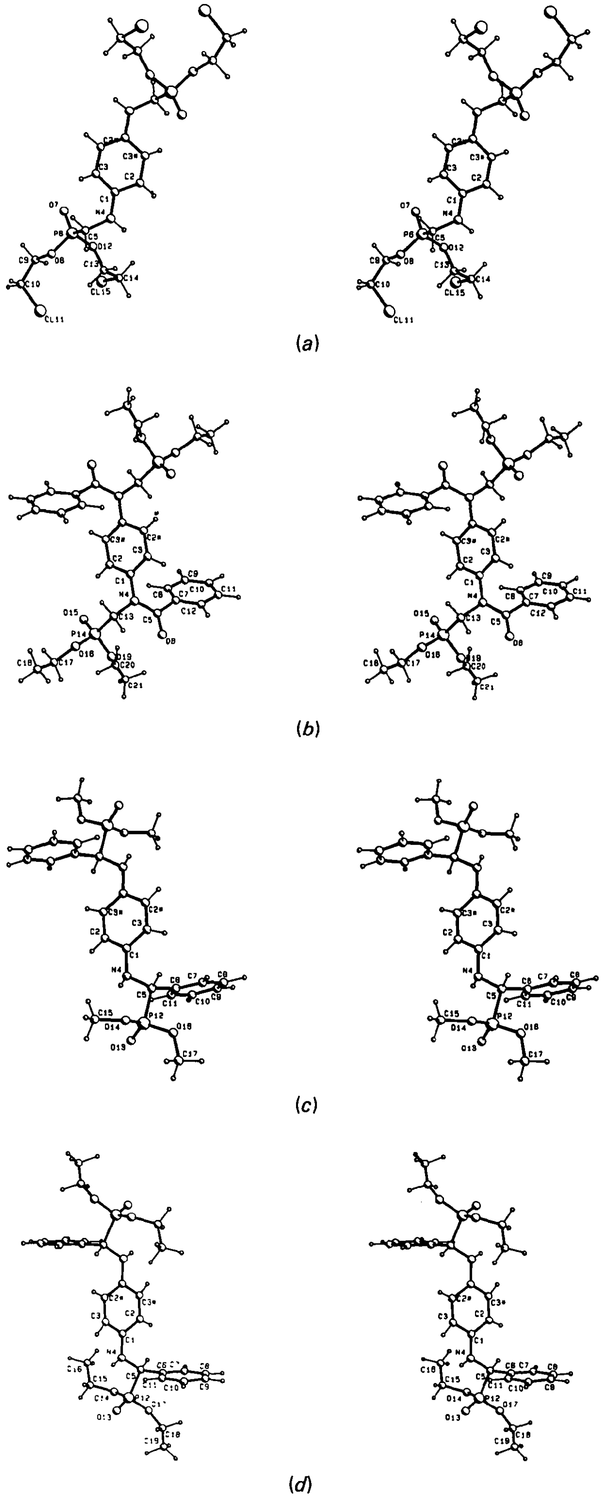

Fig. 2. (*a*)–(*d*) Stereoscopic views of compounds (II)–(V).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles for the five structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43336 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

ADAMS, W. W., FRATINI, A. V. & WIFF, D. R. (1978). *Acta Cryst.* B**34**, 954–956.
CALABRESE, J. C. & GARDNER, K. H. (1985). *Acta Cryst.* C**41**, 389–392.
HARKEMA, S. & GAYMANS, R. J. (1977). *Acta Cryst.* B**33**, 3609–3611.
KALLITSIS, J. (1986). *Eur. Polym. J.* **22**, 257–266.
KALLITSIS, J. & TSOLIS, A. (1986). *J. Appl. Polym. Sci.* In the press.
MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1984). *MULTAN*11/84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

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Methyl Carbamate

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Abstract. $C_2H_5NO_2$, $M_r = 75{\cdot}1$, triclinic, $P\bar{1}$, $a = 5{\cdot}146\ (4)$, $b = 5{\cdot}357\ (4)$, $c = 7{\cdot}147\ (6)$ Å, $\alpha = 103{\cdot}86\ (6)$, $\beta = 104{\cdot}39\ (5)$, $\gamma = 100{\cdot}65\ (8)°$, $V = 178{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}394$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}133$ mm^{-1}, $F(000) = 80$, $T = 123$ K, $R = 0{\cdot}073$ for 1603 unique observed reflections. The molecule has the expected conformation with the methyl group *trans* to the amino group with respect to the central C—O bond. The non-H atoms are planar with the exception of the methyl C which is 0·015 (2) Å out of the plane. The molecules are hydrogen-bonded into planar layers parallel to (01$\bar{2}$) by NH···O=C and CH···O< hydrogen bonds.

Introduction. The crystal structure of ethyl carbamate was reported by Braeker & Small (1967). There are no reports of crystal-structural work on the methyl compound. The structure is of interest since it contains C=O and NH_2 groups and is small enough to permit a comparison with accurate theoretical *ab initio* quantum mechanical calculations of the molecular geometry of the isolated molecule (Jeffrey, 1984, 1985). Crystals of neutron diffraction size can be obtained.

Experimental. Suitable crystals were obtained by fast evaporation of an ether solution. Since they sublime at room temperature, a crystal 0·25 × 0·3 × 0·2 mm was enclosed in a glass capillary. The intensity data were measured at 123 K by $\omega/2\theta$ scans on a CAD-4 diffractometer using Nb-filtered Mo $K\alpha$ radiation, for $-10 \le h \le 10$, $0 \le k \le 10$, $0 \le l \le 10$ to $\sin\theta/\lambda$ of 0·977 Å^{-1}. Three standard reflections $40\bar{4}$, $\bar{2}4\bar{2}$ and 214 showed a maximum deviation of $3{\cdot}9\sigma$. The crystals were soft, very mosaic, and diffracted poorly; this led to a higher-than-usual value for R; of the 3158 reflections measured up to $\theta_{\max} = 45°$, only 1603 had $F_o > 3\sigma$. The unit-cell dimensions were obtained from a least-squares fit of $\sin\theta$ values for 25 reflections with $0{\cdot}27 < \sin\theta < 0{\cdot}40$. The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) on 717 reflections of which 150 had $E > 1{\cdot}29$. Atomic scattering factors for C, O and N were those of Cromer & Waber (1965), and for H those of Stewart, Davidson & Simpson (1965). The H positions were observed on difference maps. Refinement was of $\sum w(F_o - kF_c)^2$, $w^{-1} = \sigma^2(F_o)$, with anisotropic thermal parameters for the non-H atoms and isotropic parameters for the H atoms. There were no shifts greater than $0{\cdot}01\sigma$ in any of the 66 parameters. The maximum peak height in the final difference Fourier map was 0·48 e Å^{-3}. The final agreement factors were $R = 0{\cdot}073$, $wR = 0{\cdot}071$, $S = 2{\cdot}22$. The atomic parameters are given in Table 1, the atomic notation and thermal ellipsoids are shown in Fig. 1.* The bond lengths and principal torsion and valence angles are given in Table 2.

Discussion. The O.C=O.N group is planar within 0·003 (2) Å; the methyl C atom is 0·015 (2) Å out of this plane. The methyl group is oriented with one C—H bond almost in the molecular plane. The refined positions of the methyl H atoms suggest that there is a small twist of ~10° from the *m* symmetry orientation, but this needs confirmation by neutron diffraction.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43262 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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