[sum of angles at N(1) 345·9°], while that in (III*b*) is the most pyramidal [sum of angles 337·0°]. In all three instances the four-membered rings are planar with virtually identical dimensions.

The conformation of the six-membered heterocyclic rings differs from compound to compound, although all adopt twisted and distorted boat conformations in which N(3) forms a shallow prow, and C(8) a more pronounced prow. The conformation in (III*a*) lies between that of (III*b*) and (III*c*), which follows the order of pyramidal N(1), where (III*b*) > (III*a*) > (III*c*). Although it is difficult to rationalize these conformational differences in terms of steric interactions, the flattening of N(1) in (III*c*) and the associated expansion of the C(13)—N(1)—C(2) angle have the effect of relieving interactions between the C(2) *tert*-butyl group and the aromatic ring C(9)—C(14). In this context the interbond angles at C(2) in (III*c*) compensate for this effect by showing slight expansions and contractions. No similar effect is observed for the C(8) *tert*-butyl group of (III*c*). However, the overall conformation of the molecule is such that this *tert*-butyl group projects well away from the less congested face of the molecule.

We thank Professor C. W. Rees FRS for suggesting this problem, for supplying crystalline samples and for participating in discussions.

References

Hauptman, H. & Green, E. A. (1976). *Acta Cryst.* A**32**, 45–49.

Rees, C. W. (1976). *J. Chem. Soc. Perkin Trans.* 1, pp. 2166–2169.

Rees, C. W., Storr, R. C. & Whittle, P. J. (1976). *J. Chem. Soc. Chem. Commun.* pp. 411–412.

Stewart, J. M. (1970). *Crystallographic Computing*, pp. 71–74. Edited by F. R. Ahmed. Copenhagen: Munksgaard.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland.

Acta Cryst. (1981). B**37**, 1604–1608

Structural Investigations of Ylides.
XIV.* Structures of *P*,*P*-Diphenyl-*N*-(phenylethyl)phosphinic Amide and *N*-Methyl-*P*,*P*-diphenyl-*N*-(phenylethyl)phosphinic Amide Monohydrate

By A. Forbes Cameron and Fergus D. Duncanson

*Department of Chemistry, University of Glasgow, Glasgow G*12 8*QQ, Scotland*

(*Received* 14 *October* 1980; *accepted* 12 *February* 1981)

Abstract

The structures of *P*,*P*-diphenyl-*N*-(phenylethyl)phosphinic amide (I) and *N*-methyl-*P*,*P*-diphenyl-*N*-(phenylethyl)phosphinic amide monohydrate (II) have been determined. Crystals of (I) are monoclinic, space group Pc, $Z = 4$, $a = 8{\cdot}147\,(1)$, $b = 19{\cdot}036\,(2)$, $c = 11{\cdot}563\,(1)$ Å, $\beta = 90{\cdot}10\,(8)°$, $U = 1793{\cdot}3$ Å^3. Final $R = 0{\cdot}041$ for 2315 independent diffractometer data. Crystals of (II) are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10{\cdot}911\,(1)$, $b = 7{\cdot}942\,(1)$, $c = 23{\cdot}110\,(3)$ Å, $\beta = 104{\cdot}35\,(9)°$, $U = 1940{\cdot}1$ Å^3. Final $R = 0{\cdot}039$ for 3098 independent diffractometer data. The P–N lengths are 1·643 (4) and 1·647 (5) Å in the two independent molecules of (I), and 1·646 (2) Å in (II). In each case the N atoms bonded to P are slightly pyramidal.

Introduction

We have previously described the structures of several phosphorus-containing ylides (Cameron, Hair & Morris, 1974; Cameron, Cameron & Keat, 1979). As part of a continuing interest in the structures and reactivities of these and related species, we now report analyses of the title compounds, which are ylides of the type $>P^+—O^-$.

Chemical interest in phosphinic amides stems from the roles of phosphorus-containing compounds in biological systems, and also as reagents in organic synthesis (Kenner, Moore & Ramage, 1976). The lability of the P^+—N bond is of particular significance, and it has been noted (Tysee, Bausher & Haake, 1973; Koizumi & Haake, 1973) that phosphinic amides of the type described here undergo acid hydrolysis 10^5 times faster than base hydrolysis. The latter rate is compar-

---

* Part XIII: Cameron, Cameron & Keat (1979).

0567-7408/81/081604-05$01.00

able to the rates of both base and acid hydrolyses of the corresponding carboxylic amides. To rationalize these observations, it has been suggested that acid hydrolysis of phosphinic amides occurs by protonation at N (in contrast to O protonation in carboxylic amides), with a consequent labilizing effect on the P^+–N bond possibly resulting from removal of the d_π–p_π interaction, and subsequent nucleophilic attack by water at the P atom.

Experimental

Crystal data

$C_{20}H_{20}NOP$ (I), $M_r = 321\cdot4$, $D_m = 1\cdot20$, $D_c = 1\cdot19$ Mg m^{-3}, $F(000) = 680$, Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $\mu(\text{Mo }K) = 0\cdot159$ mm^{-1}.

$C_{21}H_{22}NOP.H_2O$ (II), $M_r = 353\cdot4$, $D_m = 1\cdot17$, $D_c = 1\cdot21$ Mg m^{-3}, $F(000) = 760$, Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $\mu(\text{Mo }K) = 0\cdot160$ mm^{-1}.

Crystallographic measurements and structure determinations

Small crystals of both compounds were exposed to graphite-monochromated Mo radiation on a Hilger & Watts Y290 diffractometer, and intensity measurements were made with the θ,ω-scan technique in the range 2θ 0–60°, yielding 2315 independent reflexions [$I \geq 3\sigma_I$, $\sigma_I = \sqrt{(I + B_1 + B_2)}$] for (I), and 3098 independent reflexions ($I \geq 3\sigma_I$) for (II). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure of (I) was solved by the heavy-atom method, the coordinates of both P atoms being determined from a sharpened Patterson function. The complete structure was revealed by structure factor and electron density calculations. Atomic coordinates and thermal parameters for the two independent molecules of the asymmetric unit were refined by least-squares calculations which converged when R was 0·041.* H atom positions were for the most part calculated, and these were included as fixed contributors in the refinement. However, the N-bonded protons were located from difference syntheses, and were refined. During the refinement it became apparent that the methylene group and adjacent atoms of one of the independent molecules were slightly disordered. However, examination of successive difference syntheses only allowed alternative sites to be determined for one of the disordered atoms, the other atoms being included with exaggerated anisotropic thermal parameters.

The structure of (II) was solved with *MULTAN* (Germain, Main & Woolfson, 1971), an E map based on 250 reflexions with $|E| \geq 1\cdot56$ revealing all but a few atoms. A subsequent structure factor and electron density calculation revealed the remaining atoms, and in addition indicated the presence of one molecule of water of crystallization per molecule of phosphinic amide. Atomic parameters were refined by least-squares calculations which converged when R was

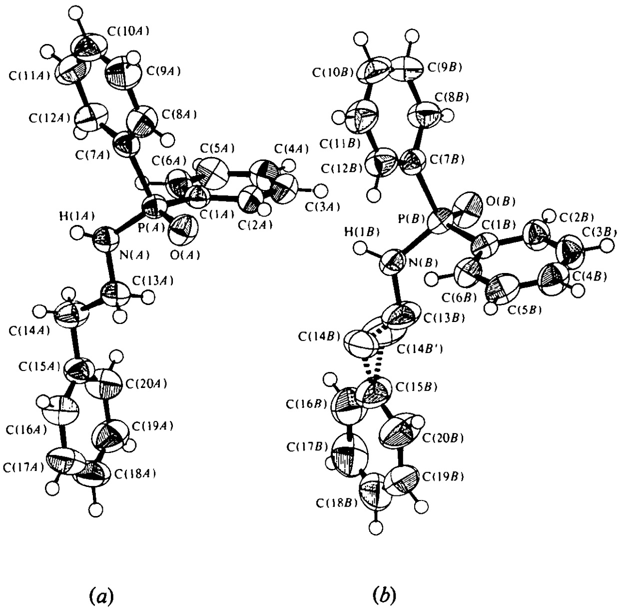


Fig. 1. Views of (a) molecule A and (b) molecule B of (I), defining the atom numbering.

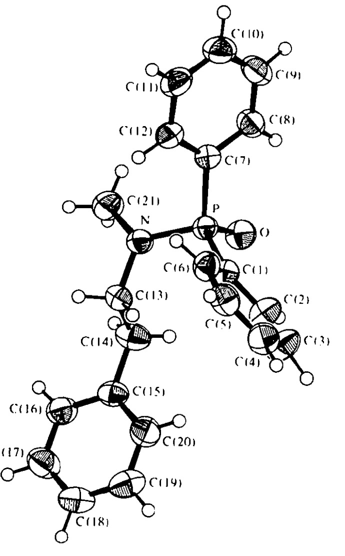


Fig. 2. A view of one molecule of (II) defining the atom numbering.

---

* Lists of structure factors, anisotropic thermal parameters and H atom parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35909 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·039.* H atoms, excluding those of the water molecule, were located from difference syntheses, and their positions were refined in later cycles.

Table 1. *Positional parameters and isotropic thermal parameters* (Å^2 × 10^3) *for* (I)

For non-hydrogen atoms $U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	U_{eq}
Molecule *A*				
P(*A*)	1·00000	0·31502 (6)	1·00000	42 (1)
O(*A*)	1·0861 (5)	0·2927 (2)	1·1068 (3)	59 (3)
N(*A*)	0·8396 (6)	0·2696 (2)	0·9570 (4)	49 (3)
C(1*A*)	1·1380 (6)	0·3122 (2)	0·8784 (4)	42 (4)
C(2*A*)	1·3058 (7)	0·3065 (3)	0·8968 (5)	54 (4)
C(3*A*)	1·4133 (8)	0·3084 (3)	0·8036 (6)	64 (4)
C(4*A*)	1·3548 (8)	0·3167 (3)	0·6940 (5)	64 (4)
C(5*A*)	1·1889 (8)	0·3209 (3)	0·6730 (5)	63 (4)
C(6*A*)	1·0806 (7)	0·3185 (3)	0·7647 (5)	52 (4)
C(7*A*)	0·9216 (6)	0·4032 (3)	1·0133 (4)	47 (4)
C(8*A*)	0·9753 (8)	0·4428 (3)	1·1065 (5)	63 (4)
C(9*A*)	0·9238 (10)	0·5110 (4)	1·1212 (7)	83 (4)
C(10*A*)	0·8198 (10)	0·5405 (3)	1·0428 (8)	78 (4)
C(11*A*)	0·7641 (9)	0·5023 (4)	0·9506 (7)	84 (4)
C(12*A*)	0·8151 (8)	0·4339 (3)	0·9355 (5)	64 (4)
C(13*A*)	0·8603 (8)	0·1935 (3)	0·9439 (5)	58 (4)
C(14*A*)	0·7171 (9)	0·1620 (3)	0·8793 (5)	67 (4)
C(15*A*)	0·7320 (8)	0·0833 (3)	0·8688 (5)	58 (4)
C(16*A*)	0·6666 (9)	0·0394 (3)	0·9528 (6)	74 (4)
C(17*A*)	0·6745 (11)	−0·0324 (4)	0·9424 (7)	84 (4)
C(18*A*)	0·7527 (11)	−0·0614 (3)	0·8521 (8)	78 (4)
C(19*A*)	0·8193 (10)	−0·0197 (4)	0·7694 (7)	86 (4)
C(20*A*)	0·8076 (10)	0·0531 (4)	0·7764 (6)	78 (4)
H(1*A*)	0·783 (5)	0·279 (2)	1·000 (4)	*
Molecule *B*				
P(*B*)	0·49624 (20)	0·28125 (7)	0·22652 (13)	48 (1)
O(*B*)	0·5836 (5)	0·2816 (2)	0·1146 (3)	64 (3)
N(*B*)	0·3348 (6)	0·2300 (2)	0·2418 (4)	56 (3)
C(1*B*)	0·6336 (6)	0·2561 (3)	0·3426 (4)	47 (5)
C(2*B*)	0·8008 (7)	0·2644 (3)	0·3273 (5)	56 (5)
C(3*B*)	0·9069 (8)	0·2476 (4)	0·4168 (6)	71 (5)
C(4*B*)	0·8481 (8)	0·2236 (4)	0·5205 (6)	70 (5)
C(5*B*)	0·6826 (9)	0·2157 (3)	0·5365 (5)	64 (5)
C(6*B*)	0·5748 (7)	0·2319 (3)	0·4472 (5)	53 (5)
C(7*B*)	0·4182 (6)	0·3675 (3)	0·2612 (4)	47 (5)
C(8*B*)	0·4643 (8)	0·4228 (3)	0·1920 (5)	66 (5)
C(9*B*)	0·4095 (10)	0·4906 (3)	0·2168 (8)	81 (5)
C(10*B*)	0·3124 (10)	0·5015 (3)	0·3116 (7)	73 (5)
C(11*B*)	0·2635 (9)	0·4462 (4)	0·3799 (6)	76 (5)
C(12*B*)	0·3187 (8)	0·3795 (3)	0·3552 (5)	64 (5)
C(13*B*)	0·3524 (12)	0·1538 (3)	0·2209 (10)	97 (5)
C(14*B*)	0·2917 (30)	0·1237 (8)	0·1334 (15)	80 (5)
C(14*B*′)	0·2192 (20)	0·1164 (7)	0·2179 (17)	100 (5)
C(15*B*)	0·2490 (11)	0·0409 (4)	0·1514 (10)	101 (5)
C(16*B*)	0·1681 (11)	0·0141 (5)	0·0578 (7)	107 (5)
C(17*B*)	0·1601 (12)	−0·0558 (6)	0·0383 (8)	104 (5)
C(18*B*)	0·2362 (11)	−0·1013 (5)	0·1103 (11)	100 (5)
C(19*B*)	0·3212 (11)	−0·0774 (4)	0·2002 (9)	100 (5)
C(20*B*)	0·3263 (12)	−0·0061 (4)	0·2240 (10)	116 (5)
H(1*B*)	0·243 (5)	0·246 (2)	0·216 (3)	†

* U_{iso} = 0·049 (12) Å^2.
† U_{iso} = 0·045 (12) Å^2.

Table 2. *Positional parameters and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for* (II)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	U_{eq}
P	0·08168 (4)	1·18587 (7)	0·12142 (2)	38 (1)
O(1)	0·04441 (13)	1·27389 (20)	0·06277 (6)	51 (1)
O(2)	0·15193 (17)	0·49276 (32)	−0·00659 (10)	90 (1)
N	0·11214 (14)	0·98289 (22)	0·12130 (7)	43 (1)
C(1)	0·22367 (16)	1·27531 (24)	0·16857 (8)	39 (2)
C(2)	0·29278 (20)	1·39134 (31)	0·14443 (10)	54 (2)
C(3)	0·40053 (23)	1·46505 (36)	0·18040 (12)	65 (2)
C(4)	0·43884 (21)	1·42618 (33)	0·23986 (11)	57 (2)
C(5)	0·37188 (20)	1·31175 (31)	0·26426 (10)	53 (2)
C(6)	0·26440 (19)	1·23639 (29)	0·22905 (9)	47 (2)
C(7)	−0·04158 (16)	1·20678 (25)	0·16067 (8)	41 (2)
C(8)	−0·13140 (20)	1·33276 (30)	0·14335 (10)	51 (2)
C(9)	−0·22429 (22)	1·35742 (34)	0·17403 (11)	61 (2)
C(10)	−0·22709 (22)	1·25988 (35)	0·22242 (12)	65 (2)
C(11)	−0·13865 (23)	1·13507 (34)	0·24036 (12)	63 (2)
C(12)	−0·04648 (20)	1·10667 (30)	0·20951 (10)	52 (2)
C(13)	0·23784 (18)	0·92225 (30)	0·11828 (9)	44 (2)
C(14)	0·27101 (22)	0·94591 (41)	0·05817 (10)	56 (2)
C(15)	0·40477 (19)	0·89024 (30)	0·06201 (9)	49 (2)
C(16)	0·43180 (20)	0·72622 (32)	0·04913 (10)	57 (2)
C(17)	0·55548 (23)	0·67567 (38)	0·05374 (12)	65 (2)
C(18)	0·65316 (22)	0·78794 (38)	0·07098 (11)	63 (2)
C(19)	0·62837 (23)	0·94996 (40)	0·08442 (12)	66 (2)
C(20)	0·50493 (23)	1·00097 (36)	0·08007 (11)	60 (2)
C(21)	0·00731 (23)	0·87074 (34)	0·09201 (15)	62 (2)

Figs. 1 and 2 show views of the two independent molecules of (I), and of the molecule of (II), and also define the atom numbering. Tables 1 and 2 contain atomic coordinates for (I) and (II) respectively, while Table 3 presents details of the molecular geometries.

Discussion

The analyses of (I) and (II) reveal several features which may possibly correlate with the enhanced rate of acid relative to base hydrolysis. Thus, the P—N bonds in (I*A*, *B*) and (II) have experimentally identical lengths of 1·643 (4), 1·647 (5) and 1·646 (2) Å. A value of 1·681 (6) Å is observed for the corresponding bond in (III) by Mazhur-ul-Haque & Caughlan (1976), who used an empirical relationship to suggest a P—N bond order of 1·36. Rather shorter P(O)—N lengths of 1·557 (2) and 1·605 (2) Å are observed in (IV) and (V) respectively (Cameron, Cameron & Keat, 1979). The latter values are compatible with the different abilities of dichloro- and diphenylphosphinoyl groups to compete for lone pairs of electrons on N, and are almost certainly indicative of a substantial degree of P—N double bonding. A plausible conclusion for (I) and (II) is that there exists some degree of multiple bonding, but not to the extent that the N atoms become unattractive for protonation, which then removes the

---

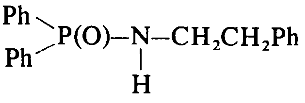
* See previous footnote.

Table 3. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

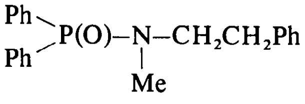
	(I*A*)	(I*B*)	(II)
P–O	1·481 (4)	1·478 (4)	1·489 (1)
P–N	1·643 (4)	1·647 (5)	1·646 (2)
P–C(1)	1·803 (5)	1·810 (5)	1·804 (2)
P–C(7)	1·802 (5)	1·806 (5)	1·807 (2)
N–C(3)	1·467 (7)	1·477 (8)	1·472 (3)
H–N(1)	0·82 (4)	0·86 (4)	–
N–C(21)	–	–	1·475 (3)
C(13)–C(14)	1·509 (9)	*	1·532 (3)
C(14)–C(15)	1·508 (8)	*	1·506 (3)
C(15)–C(16)	1·389 (9)	1·365 (13)	1·384 (3)
C(16)–C(17)	1·374 (10)	1·351 (15)	1·387 (4)
C(17)–C(18)	1·343 (12)	1·352 (15)	1·371 (4)
C(18)–C(19)	1·357 (11)	1·329 (15)	1·366 (4)
C(19)–C(20)	1·391 (10)	1·386 (12)	1·386 (4)
C(20)–C(15)	1·362 (9)	1·378 (13)	1·384 (3)
C(1)–C(2)	1·388 (7)	1·383 (8)	1·392 (3)
C(2)–C(3)	1·390 (9)	1·385 (9)	1·390 (4)
C(3)–C(4)	1·362 (9)	1·370 (9)	1·369 (4)
C(4)–C(5)	1·375 (9)	1·369 (10)	1·372 (3)
C(5)–C(6)	1·381 (8)	1·390 (9)	1·381 (3)
C(6)–C(1)	1·400 (7)	1·381 (7)	1·393 (3)
C(7)–C(8)	1·386 (8)	1·374 (8)	1·388 (3)
C(8)–C(9)	1·375 (9)	1·395 (9)	1·387 (3)
C(19)–C(10)	1·362 (11)	1·369 (12)	1·367 (4)
C(10)–C(11)	1·367 (11)	1·375 (10)	1·374 (4)
C(11)–C(12)	1·378 (9)	1·377 (9)	1·388 (3)
C(12)–C(7)	1·379 (8)	1·375 (8)	1·392 (3)
O–P–N	118·5 (2)	118·8 (3)	117·9 (1)
O–P–C(2)	110·3 (2)	110·6 (2)	111·4 (1)
O–P–C(7)	111·3 (2)	111·1 (2)	110·2 (1)
N–P–C(1)	104·1 (2)	104·9 (2)	104·1 (1)
N–P–C(7)	103·5 (2)	103·5 (2)	105·5 (1)
C(1)–P–C(7)	108·4 (2)	107·1 (2)	107·2 (1)
P–N–C(13)	117·4 (4)	119·1 (5)	120·8 (1)
P–N–H(1)	107·9 (30)	116·2 (28)	
H(1)–N–C(13)	111·5 (30)	112·2 (28)	
P–N–C(21)			117·3 (1)
C(21)–N–C(13)			114·0 (1)
N–C(13)–C(14)	110·8 (5)	*	115·8 (2)
C(13)–C(14)–C(15)	111·9 (5)	*	110·7 (2)
C(14)–C(15)–C(16)	120·7 (6)	*	121·2 (2)
C(15)–C(16)–C(17)	121·3 (6)	121·6 (9)	120·7 (2)
C(16)–C(17)–C(18)	119·9 (7)	120·5 (9)	120·4 (2)
C(17)–C(18)–C(19)	120·0 (6)	120·0 (9)	119·7 (2)
C(18)–C(19)–C(20)	120·9 (7)	120·5 (9)	120·2 (2)
C(19)–C(20)–C(15)	119·9 (6)	120·1 (8)	121·1 (2)
C(20)–C(15)–C(16)	118·0 (6)	117·4 (8)	117·9 (2)
C(14)–C(15)–C(20)	121·3 (6)	*	120·8 (2)
P–C(1)–C(2)	119·9 (4)	118·9 (4)	119·2 (1)
P–C(1)–C(6)	121·5 (4)	121·5 (4)	122·1 (1)
C(2)–C(1)–C(6)	118·6 (5)	119·6 (5)	118·6 (2)
C(1)–C(2)–C(3)	120·0 (5)	119·4 (5)	120·1 (2)
C(2)–C(3)–C(4)	120·3 (6)	120·9 (6)	120·5 (2)
C(3)–C(4)–C(5)	120·9 (6)	120·0 (6)	120·1 (2)
C(4)–C(5)–C(6)	119·4 (5)	119·8 (5)	120·3 (2)
C(5)–C(6)–C(1)	120·7 (5)	120·3 (5)	120·4 (2)
P–C(7)–C(8)	117·5 (4)	118·0 (4)	118·8 (1)
P–C(7)–C(12)	124·2 (4)	122·3 (4)	122·5 (1)
C(8)–C(7)–C(12)	118·3 (5)	119·7 (5)	118·6 (2)
C(7)–C(8)–C(9)	120·9 (6)	120·0 (6)	120·5 (2)
C(8)–C(9)–C(10)	119·8 (7)	119·4 (6)	120·4 (2)
C(9)–C(10)–C(11)	120·3 (7)	120·8 (6)	120·0 (2)
C(10)–C(11)–C(12)	120·1 (7)	119·4 (6)	120·4 (2)
C(11)–C(12)–C(7)	120·5 (6)	120·7 (6)	120·1 (2)
O–P–C(1)–C(2)	–14·3	22·3	–9·9
O–P–C(7)–C(8)	12·0	–8·2	–18·4
O–P–N–C(13)	–52·9	56·8	83·9
O–P–N–C(21)	–	–	–63·2
N–P–C(1)–C(2)	–142·4	151·5	118·2
N–P–C(7)–C(8)	140·3	–136·8	–146·6
C(1)–P–N–C(13)	70·0	–67·5	–40·1
C(1)–P–N–C(21)	–	–	172·9
C(7)–P–N–C(13)	–176·7	–179·6	–152·7
C(7)–P–N–C(21)	–	–	60·2
P–N–C(13)–C(14)	–167·2	*	–71·3
C(21)–N–C(13)–C(14)	–	–	76·8
N–C(13)–C(14)–C(15)	–177·7	*	176·1
C(13)–C(14)–C(15)–C(16)	90·0	*	90·5
C(13)–C(14)–C(15)–C(20)	–91·0	*	–87·8
O–P–N–H(1)	74 (3)	–83 (3)	–
Mean e.s.d. [excluding final angle involving H(1)]	0·5	0·8	0·2

* Value affected by disorder.

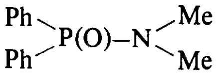
possibility of multiple bonding completely and hence labilizes the P–N bond.


$\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}\!>\!\mathrm{P(O)}{-}\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}{-}\mathrm{CH_2CH_2Ph}$

(I)


$\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}\!>\!\mathrm{P(O)}{-}\underset{\mathrm{Me}}{\underset{|}{\mathrm{N}}}{-}\mathrm{CH_2CH_2Ph}$

(II)


$\begin{smallmatrix}\mathrm{Ph}\\ \mathrm{Ph}\end{smallmatrix}\!>\!\mathrm{P(O)}{-}\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{Me}\\ \mathrm{Me}\end{smallmatrix}$

(III)

$\mathrm{(Ph)_3P^+{-}N^-{-}P(O)Cl_2}$

(IV)

$\mathrm{(Ph)_3P^+{-}N^-{-}P(O)Ph_2}$

(V)

In conjunction with the above conclusion, the N atoms in (I*A*, *B*) and (II) are all markedly non-planar (sum of angles at N: 337, 347 and 352° respectively), although it should be noted that in (I) this observation is based on the relatively inaccurate positions of the N-bonded H atoms (located from difference syntheses and refined by least squares). However, the same effect is observed in (III), in which the sum of the angles at N is 349°. The postulated N protonation of acid hydrolysis would thus occur at atoms which are already slightly pyramidal.

Of the other features of the geometries of (I) and (II), the P–O lengths of 1·481 (4), 1·478 (4) and 1·489 (1) Å compare well with values for this bond observed alsewhere (*e.g.* Cameron, Cameron & Keat, 1979). The P atoms exhibit distorted tetrahedral geometries, in which the O–P–N angles (average 118·4°) are the largest, and the N–P–C angles (average 104·3°) the smallest. The conformation about the P–N bond is staggered in each case, with the P–O bond *trans* with respect to the site of the putative N protonation.

Molecules of (I) are linked in the solid state by N–H···O hydrogen bonding, while the water of crystallization fulfils a similar role in the structure of (II).

References

Cameron, A. F., Cameron, I. R. & Keat, R. (1979). *Acta Cryst.* B**35**, 1373–1377.

Cameron, A. F., Hair, N. J. & Morris, D. G. (1974). *Acta Cryst.* B**30**, 221–225.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Kenner, G. W., Moore, G. A. & Ramage, R. (1976). *Tetrahedron Lett.* pp. 3623–3626.

Koizumi T. & Haake, P. (1973). *J. Am. Chem. Soc.* **95**, 8073–8079.

Mazhar-ul-Haque & Caughlan, C. N. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1101–1104.

Tysee, D. A., Bausher, L. P. & Haake, P. (1973). *J. Am. Chem. Soc.* **95**, 8066–8072.

Acta Cryst. (1981). B**37**, 1608–1613

Structural Investigations of Ylides.
XV.* Structures of *S*,*S*-Dimethyl-*N*-(*m*-nitrophenyl)sulphimide, *S*,*S*-Dimethyl-*N*-(*p*-nitrophenyl)sulphimide and the Picrate Salt of *N*-(*p*-Chlorophenyl)-*S*,*S*-dimethylsulphimide

By A. Forbes Cameron, Andrew A. Freer and Abraham Maltz

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 14 *October* 1980; *accepted* 12 *February* 1981)

Abstract

The structure of *S*,*S*-dimethyl-*N*-(*m*-nitrophenyl)-sulphimide (I), of its *p*-nitro analogue (II) and of the picrate salt of the *p*-chloro analogue (III) have been determined. Crystals of (I) are orthorhombic, space group $P2_12_12_1$, with a = 13·663 (3), b = 13·850 (3), c = 5·008 (1) Å, Z = 4, U = 947·68 Å^3. (II) is monoclinic, space group $P2_1/c$, with a = 4·811 (1), b = 9·874 (2), c = 19·947 (4) Å, β = 97·45 (3)°, Z = 4, U = 939·6 Å^3. Crystals of (III) are also monoclinic, space group $P2_1/n$, with a = 7·924 (1), b = 9·406 (1), c = 23·078 (2) Å, β = 92·19 (6)°, Z = 4, U = 1718·8 Å^3. For 1348, 868 and 3687 independent diffractometer data for (I), (II) and (III), respectively, the final R = 0·030 for (I), 0·052 for (II) and 0·033 for (III). The S–N lengths are 1·622 (2) in (I), 1·640 (4) in (II) and 1·631 (1) Å in (III), while the N–C(aryl) lengths are, respectively, 1·391 (2), 1·366 (6) and 1·415 (2) Å. The solid-state conformations of (I) and (II) are virtually identical, but differ from that of (III). The analysis of (III) confirms that salt formation occurs with protonation of the ylide at N, the latter atom being planar and trigonal.

Introduction

The stabilities and reactivities of stabilized ylides, X^+-Y^--R, are in part determined by the extent to which the electron pair(s) on Y^- interact both with the onium group X^+, and also with the stabilizing group R. We have previously described the structures of several second-row ylides including two *N*-sulphonyliminosulphuranes ($>S^+-N^--SO_2R$) (Cameron, Cameron, Campbell & Johnson, 1976; Cameron, Hair & Morris, 1973) and an *N*-acyliminosulphurane ($>S^+-N^--COR$) (Cameron, Duncanson & Morris, 1976). *N*-Sulphonyl and *N*-acyl examples are relatively unreactive and long-lived at room temperature, whereas *N*-aryliminosulphuranes ($>S^+-N^--C_6H_4-Y$) with strongly electron-withdrawing groups (Y = CN, NO_2) on the aromatic ring are only moderately stable (1–12 months at room temperature), and halogenated examples are hygroscopic and decompose within a few days at room temperature (Varkey, Whitfield & Swern, 1974). Thus crystals of (I) and (II) prepared for the analyses survived for several months, but are nevertheless sufficiently reactive to be of chemical interest. In a subsequent publication (A. F. Cameron & A. Maltz, to be published), we shall report the structures of several of their reaction products. In contrast to (I) and (II), *N*-(*p*-chlorophenyl)-*S*,*S*-dimethylsulphimide is

---

* Part XIV: Cameron & Duncanson (1981).

0567-7408/81/081608-06\$01.00