Structural Investigations of Ylides. Part I. Crystal and Molecular Structures of Trimethylammoniobenzamidate and Trimethylammonionitramidate: Two Stabilised Nitrogen–Nitrogen Ylides [1]

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Crystal structure analyses of the title compounds (IIa) and (III) have been carried out with diffractometer data. Both were solved by direct methods and refined by least-squares techniques to R 0·072 [(IIa), 977 reflexions] and 0·078 [(III), 378 reflexions]. Crystal data are: (IIa), monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11{\cdot}620(10)$, $b = 7{\cdot}928(6)$, $c = 11{\cdot}454(10)$ Å, $\beta = 113{\cdot}75(3)°$; (III), orthorhombic, space group $Pnma$, $Z = 4$, $a = 12{\cdot}245(6)$, $b = 6{\cdot}718(3)$, $c = 7{\cdot}099(5)$ Å. The results of the analyses indicate significant charge delocalisation on the oxygen atoms of the stabilising benzoyl- and nitro-groups respectively. In both molecules the quaternary nitrogen and delocalised anionic moieties adopt a *syn*-planar relationship, this conformation resulting in possible interactions between oxygen and methyl-hydrogen atoms in each case. In compounds (II; a—d) temperature invariant n.m.r. spectra, consistent with a single conformation in solution, were obtained.

YLIDES of first-row elements in general contain a quaternary ammonium group vicinal to an electronegative atom X as in (I),[2] the simplest compounds of this type being the amine oxides (I; X = O), although the intermediacy of ylides of the type $Ph_2\bar{C}{\cdot}\overset{+}{O}HR$ has been recently demonstrated in the reaction of diphenylcarbene with alcohols.[3] However, in cases where X is either nitrogen or carbon, the ylides require further stabilisation, and this is usually achieved by the presence of electron-withdrawing groups such as $-CHO$, $-COMe$, $-COPh$, $-CO_2Me$, $-NO_2$, or $-SO_2Ar$, bonded to the electronegative atom X. In ylides of this type although formal bonding of the d_π–p_π type between the 'onium nitrogen and vicinal electronegative atoms is not possible, the $\overset{+}{N}$–$\bar{X}$ bond-order being formally restricted

$$R_3\overset{+}{N}-\bar{X} \qquad Me_3\overset{+}{N}-\bar{N}-R \qquad Me_3\overset{+}{N}-\bar{N}-NO_2$$

(I) (II) (III)

	R
a;	COPh
b;	CHO
c;	COMe
d;	CO_2Me

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[1] Preliminary publication, A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *Chem. Comm.*, 1971, 725.

[2] A. W. Johnson, 'Ylid Chemistry,' Academic Press, London, 1966.

[3] D. Bethell, A. R. Newall, and D. Whittaker, *J. Chem. Soc.* (*B*), 1971, 23.

to unity, there exists the possibility of the negative charge being delocalised through the electronegative moiety.

As part of an examination of the bonding, charge distributions, and conformations of first-row ylides, we have determined the crystal structures of the *N*-trimethylammonioamidates (IIa)[4] and (III),[5] which are representative of the class of ylides (I; X = N−).

EXPERIMENTAL

Crystal Data.—(i) (IIa), $C_{10}H_{14}N_2O$, $M = 178{\cdot}2$. Monoclinic, $a = 11{\cdot}620(10)$, $b = 7{\cdot}928(6)$, $c = 11{\cdot}454(10)$ Å, $\beta = 113{\cdot}75(3)°$, $U = 965{\cdot}8$ Å^3, $D_m = 1{\cdot}21$ (by flotation), $Z = 4$, $D_c = 1{\cdot}23$, $F(000) = 384$. Space group $P2_1/c$ (C^5_{2h}). Mo-K_α *X*-radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = $0{\cdot}87$ cm^{-1}.

(ii) (III), $C_3H_9N_3O_2$, $M = 119{\cdot}1$. Orthorhombic, $a = 12{\cdot}245(6)$, $b = 6{\cdot}718(3)$, $c = 7{\cdot}099(5)$ Å, $U = 574{\cdot}1$ Å^3, $D_m = 1{\cdot}36$ (by flotation), $Z = 4$, $D_c = 1{\cdot}38$, $F(000) = 256$. Space group *Pnma* (D^{16}_{2h}). μ(Mo-K_α) = $1{\cdot}23$ cm^{-1}.

Crystallographic Measurements.—The unit-cell parameters of both compounds were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation, and from precession photographs taken with Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation, the values later being refined by least-squares techniques before the diffractometer data collections. Although the systematic absences in the $0k0$ and $h0l$ spectra uniquely determine the space group of (IIa) as $P2_1/c$, the absences in the spectra of (III) result in the choice of space groups *Pnma* and $Pna2_1$. The correctness of the former space group was indicated first by statistical tests, and later by a trial refinement using the non-restrictive symmetry of space group $Pna2_1$. As a consequence, molecules of (III) in the solid state are restricted to possess crystallographic mirror symmetry, the mirror plane containing the atoms O′(1), O′(2), N′(1), N′(2), N′(3), and C′(1).

Intensity measurements were made on a Hilger and Watts Y 290 computer-controlled diffractometer with Sr/Zr balanced filters [for (IIa)] and Zr filters [for (III)]. For (IIa) a flat hexagon 0·6 × 0·5 × 0·2 mm was mounted about *b*. 977 independent reflexions were obtained by the ω-scan technique in the range 2θ 0—44°. For (III) a flat plate 0·4 × 0·2 × 0·05 was mounted about *c*. 378 independent reflexions ($I > 3\sigma_I$) were obtained by the 2θ-scan technique in the range 2θ 0—50°. Both sets of intensity data were corrected for the appropriate Lorentz and polarisation factors, but absorption effects were considered negligible in both cases and were ignored.

Structure Determinations.—Both structures were solved by the application of the symbolic addition method,[6] using programs developed by Stewart *et al.*,[7] and modified by the Glasgow group. Initial *E*-maps based on 140 reflexions for (IIa) and 80 reflexions for (III), completely revealed both structures, and improved co-ordinates for use in the least-squares refinements were obtained in each case by two rounds of structure-factor and electron-density calculations. After each structure-factor calculation, in which overall isotropic thermal parameters $U_{iso} = 0{\cdot}05$ Å^2 were assumed, the two sets of data were placed on approximate absolute scales by equating $k\Sigma|F_o|$ and $\Sigma|F_c|$.

Structure Refinements.—The positional, vibrational, and overall-scale parameters for both structures were refined by three-dimensional least-squares calculations, which in the case of (IIa) converged after 15 cycles when *R* was 0·072 and R' ($= \Sigma w\Delta^2/\Sigma w|F_o|^2$) was 0·005, and for (III) converged after 10 cycles when *R* was 0·078 and R' was 0·007. Details of both refinements are given in Table 1.

TABLE 1

Course of refinement

(*a*) For (IIa)

Cycles	Parameters refined	Final *R*	Final *R′*
1—3	*x*, *y*, *z*, U_{iso} for O, N, C, overall scale-factor, full matrix, unit weights.	0·164	0·0221
4—9	*x*, *y*, *z*, U_{ij} for O, N, C, overall scale-factor, full matrix, weighting scheme adjusted, hydrogen atom contributions included but not refined.	0·083	0·0070
10—12	*x*, *y*, *z*, U_{iso} for H only, overall scale-factor, full matrix, weighting scheme applied, contributions of other atoms included but not refined.	0·076	0·0057
13—15	*x*, *y*, *z*, U_{ij} for O, N, C, *x*, *y*, *z*, U_{iso} for H, overall scale-factor, Block diagonal, weighting scheme applied.	0·072	0·0053

(*b*) For (III)

Cycles	Parameters refined	Final *R*	Final *R′*
1—4	*x*, *y*, *z*, U_{iso} for O, N, C,* overall scale-factor, full matrix, unit weights.	0·136	0·0189
5—10	*x*, *y*, *z*, U_{ij} for O, N, C,* *x*, *y*, *z*, U_{iso}* for H, overall scale-factor, full matrix, unit weights.	0·078	0·0066

* The appropriate restrictions were applied for atoms lying on the crystallographic mirror plane at *y* = 0·2500.

Difference syntheses calculated after the preliminary cycles of both refinements revealed the positions of all the hydrogen atoms of the two structures. Positional and isotropic thermal parameters for the hydrogen atoms were then refined in later cycles. In all the cycles of the refinement of (IIa), a weighting scheme was applied of the form: $\sqrt{w} = \{[1 - \exp(-p_1(\sin\theta/\lambda)^2]/[1 + p_2|F_o| + p_3|F_o|^2]\}^{\frac{1}{2}}$. Initially the *p* parameters were chosen to give unit weights to all reflexions, but were adjusted in later cycles according to an ($|F_o|$ and $\sin\theta/\lambda$) analysis of $w\Delta^2$, the final values being: $p_1 = 500$, $p_2 = 0{\cdot}01$, and $p_3 = 0{\cdot}0001$. Throughout the refinement of (III) it was not found necessary to apply other than unit weights to the data, and no weighting scheme was used.

On the convergence of both refinements, the calculation of electron-density distributions and difference syntheses revealed no errors in the structures, and the refinements were therefore considered complete. Tables of observed and final calculated structure factors * appear in Supplementary Publication No. SUP 20377 (5 pp., 1 microfiche).†

Final fractional co-ordinates and thermal parameters for both compounds are given in Table 2, and Table 3 contains all bond lengths, valency angles, and pertinent

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* In all structure-factor calculations, the atomic scattering factors used are taken from ref. 8.

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[4] M. S. Gibson and A. W. Murray, *J. Chem. Soc.*, 1965, 880.

[5] J. Epsztajn and A. R. Katritzky, *Tetrahedron Letters*, 1969, 4739.

[6] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[7] J. M. Stewart, Technical Report TR-67-58, University of Maryland, 1967.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

(*a*) Fractional co-ordinates and isotropic thermal parameters (Å²) for hydrogen atoms for (IIa)

	x/a	y/b	z/c	U_{iso}
O(1)	0·57612(28)	0·56779(43)	0·18706(31)	
N(1)	0·73327(33)	0·79510(43)	0·35623(33)	
N(2)	0·78068(33)	0·64719(44)	0·31187(32)	
C(1)	0·84956(52)	0·87933(73)	0·44653(54)	
C(2)	0·66483(54)	0·91490(64)	0·25102(48)	
C(3)	0·65195(51)	0·74764(65)	0·42487(46)	
C(4)	0·69233(41)	0·55200(52)	0·23021(37)	
C(5)	0·74644(39)	0·40627(50)	0·18261(37)	
C(6)	0·87096(41)	0·35595(56)	0·24328(39)	
C(7)	0·91848(43)	0·23305(57)	0·19039(43)	
C(8)	0·84249(47)	0·15877(57)	0·07625(43)	
C(9)	0·71855(45)	0·20743(57)	0·01660(40)	
C(10)	0·66940(43)	0·32943(54)	0·06963(40)	
H(11)	0·8255(43)	0·9797(64)	0·4847(43)	0·065(16)
H(12)	0·8960(51)	0·9145(74)	0·3925(51)	0·097(20)
H(13)	0·8779(40)	0·7870(56)	0·5186(40)	0·050(14)
H(21)	0·5922(48)	0·8530(70)	0·1896(48)	0·083(18)
H(22)	0·6395(44)	1·0099(65)	0·2857(45)	0·068(16)
H(23)	0·7314(48)	0·9535(70)	0·2145(48)	0·089(19)
H(31)	0·5748(46)	0·6847(67)	0·3574(46)	0·076(17)
H(32)	0·6313(35)	0·8616(50)	0·4586(35)	0·071(12)
H(33)	0·7121(45)	0·6691(66)	0·4939(45)	0·076(17)
H(6)	0·9204(35)	0·4092(50)	0·3271(35)	0·032(12)
H(7)	1·0121(46)	0·1981(62)	0·2363(46)	0·064(16)
H(8)	0·8714(41)	0·0694(59)	0·0321(41)	0·055(14)
H(9)	0·6635(38)	0·1495(54)	−0·0613(37)	0·039(12)
H(10)	0·5836(45)	0·3667(68)	0·0273(47)	0·077(18)

(*b*) Anisotropic temperature factors * (Å²) for (IIa)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	0·0566	0·0805	0·0841	−0·0493	0·0419	−0·0027
N(1)	0·0653	0·0503	0·0600	−0·0169	0·0466	0·0032
N(2)	0·0641	0·0510	0·0610	−0·0223	0·0487	0·0072
C(1)	0·0858	0·0846	0·1030	−0·0930	0·0599	−0·0273
C(2)	0·1179	0·0600	0·0794	0·0228	0·0916	0·0479
C(3)	0·1072	0·0716	0·0730	−0·0047	0·1147	0·0069
C(4)	0·0721	0·0479	0·0476	0·0034	0·0454	−0·0070
C(5)	0·0649	0·0410	0·0511	0·0010	0·0546	0·0019
C(6)	0·0654	0·0559	0·0533	0·0002	0·0441	0·0087
C(7)	0·0688	0·0543	0·0699	−0·0018	0·0583	0·0051
C(8)	0·0890	0·0505	0·0673	−0·0072	0·0765	0·0024
C(9)	0·0846	0·0523	0·0551	−0·0071	0·0520	−0·0160
C(10)	0·0749	0·0496	0·0547	−0·0064	0·0534	−0·0088

Mean estimated standard deviations (Å²)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0·0019	0·0023	0·0022	0·0038	0·0033	0·0035
N	0·0024	0·0021.	0·0022	0·0036	0·0037	0·0038
C	0·0034	0·0028	0·0029	0·0048	0·0052	0·0052

(*c*) Fractional co-ordinates and isotropic thermal parameters (Å²) for hydrogen atoms for (III)

	x/a	y/b	z/c	U_{iso}
O′(1)	0·49169(45)	0·25000	0·50415(89)	
O′(2)	0·37461(53)	0·25000	0·26996(78)	
N′(1)	0·33316(43)	0·25000	0·75728(78)	
N′(2)	0·30833(43)	0·25000	0·55464(74)	
N′(3)	0·39474(53)	0·25000	0·44281(77)	
C′(1)	0·22237(62)	0·25000	0·84537(119)	
C′(2)	0·39067(50)	0·06268(97)	0·81910(82)	
H′(11)	0·2353(94)	0·2500	0·9976(159)	0·058(30)
H′(12)	0·1785(47)	0·1328(89)	0·7959(85)	0·033(18)
H′(21)	0·4598(40)	0·0594(76)	0·7610(73)	0·011(13)
H′(22)	0·4001(47)	0·0481(88)	0·9732(81)	0·025(16)
H′(23)	0·3316(59)	−0·0573(110)	0·7748(107)	0·060(25)

(*d*) Anisotropic temperature factors * (Å²) for (III)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O′(1)	0·0336	0·0642	0·0540	0·0000	0·0190	0·0000
O′(2)	0·0647	0·0634	0·0352	0·0000	0·0036	0·0000
N′(1)	0·0280	0·0351	0·0289	0·0000	0·0134	0·0000
N′(2)	0·0291	0·0392	0·0275	0·0000	−0·0091	0·0000
N′(3)	0·0491	0·0350	0·0260	0·0000	0·0143	0·0000
C′(1)	0·0358	0·0469	0·0457	0·0000	0·0334	0·0000
C′(2)	0·0512	0·0520	0·0455	0·0303	0·0041	0·0384

Mean estimated standard deviations (Å²)

TABLE 2 (*Continued*)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0·0031	0·0037	0·0030		0·0050	
N	0·0028	0·0029	0·0025		0·0044	
C	0·0032	0·0036	0·0034	0·0053	0·0054	0·0056

* The anisotropic temperature factor is in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances (IIa)

O(1)–C(4)	1·243(5)	C(5)–C(10)	1·383(6)
N(1)–N(2)	1·471(5)	C(6)–C(7)	1·375(6)
N(1)–C(1)	1·489(7)	C(7)–C(8)	1·380(7)
N(1)–C(2)	1·488(6)	C(8)–C(9)	1·377(7)
N(1)–C(3)	1·500(6)	C(9)–C(10)	1·382(6)
N(2)–C(4)	1·313(6)	Mean C–H(Ph)	0·99(5)
C(4)–C(5)	1·518(6)	Mean C–H(Me)	1·02(5)
C(5)–C(6)	1·388(6)		

(*b*) Interbond angles (IIa)

N(2)–N(1)–C(1)	103·7(3)	N(2)–C(4)–C(5)	112·0(4)
N(2)–N(1)–C(2)	112·5(3)	C(4)–C(5)–C(6)	122·6(4)
N(2)–N(1)–C(3)	112·6(3)	C(4)–C(5)–C(10)	117·8(4)
C(1)–N(1)–C(2)	108·4(4)	C(6)–C(5)–C(10)	119·5(4)
C(1)–N(1)–C(3)	109·6(4)	C(5)–C(6)–C(7)	120·4(4)
C(2)–N(1)–C(3)	109·9(4)	C(6)–C(7)–C(8)	120·2(4)
N(1)–N(2)–C(4)	114·2(3)	C(7)–C(8)–C(9)	119·5(4)
O(1)–C(4)–N(2)	129·6(4)	C(8)–C(9)–C(10)	120·9(4)
O(1)–C(4)–C(5)	118·3(4)	C(5)–C(10)–C(9)	119·5(4)

(*c*) Intramolecular non-bonded distances (IIa)

O(1) ··· N(1)	2·74	N(2) ··· C(10)	3·58
O(1) ··· C(2)	2·93	C(1) ··· C(4)	3·54
O(1) ··· C(3)	2·88	C(2) ··· C(4)	2·92
O(1) ··· C(6)	3·63	C(3) ··· C(4)	2·90
O(1) ··· C(10)	2·78	C(4) ··· C(7)	3·80
O(1) ··· H(21)	2·27	C(4) ··· C(9)	3·76
O(1) ··· H(31)	2·17	C(5) ··· C(8)	2·77
N(1) ··· C(5)	3·71	C(6) ··· C(9)	2·75
N(2) ··· C(6)	2·78	C(7) ··· C(10)	2·77

(*d*) Intermolecular distances (IIa)

O(1) ··· C(2$^{\mathrm{I}}$)	3·38	C(1) ··· C(10$^{\mathrm{V}}$)	3·75
O(1) ··· C(3$^{\mathrm{I}}$)	3·52	C(2) ··· C(9$^{\mathrm{VI}}$)	3·78
O(1) ··· C(3$^{\mathrm{II}}$)	3·75	C(3) ··· C(4$^{\mathrm{V}}$)	3·69
O(1) ··· C(9$^{\mathrm{III}}$)	3·73	C(3) ··· C(9$^{\mathrm{IV}}$)	3·75
O(1) ··· C(10$^{\mathrm{III}}$)	3·27	C(3) ··· C(10$^{\mathrm{V}}$)	3·71
N(2) ··· C(8$^{\mathrm{IV}}$)	3·72	C(4) ··· C(9$^{\mathrm{IV}}$)	3·78
C(1) ··· C(5$^{\mathrm{V}}$)	3·77		

Roman numerals as superscripts refer to the equivalent positions which should be applied to the co-ordinates of the second atom:

I $1-x, \frac{1}{2}+y, \frac{3}{2}-z$
II $x, \frac{3}{2}-y, -\frac{1}{2}+z$
III $1-x, 1-y, -z$
IV $x, \frac{1}{2}-y, \frac{1}{2}+z$
V $x, \frac{3}{2}-y, \frac{1}{2}+z$
VI $x, 1+y, z$

(*e*) Bonded distances (III)

O′(1)–N′(3)	1·265(8)	N′(1)–C′(2)	1·507(7)
O′(2)–N′(3)	1·252(8)	N′(2)–N′(3)	1·323(8)
N′(1)–N′(2)	1·470(8)	Average C–H	1·05(6)
N′(1)–C′(1)	1·490(9)		

(*f*) Interbond angles (III)

N′(2)–N′(1)–C′(1)	102·8(5)	N′(1)–N′(2)–N′(3)	115·0(5)
N′(2)–N′(1)–C′(2)	112·4(3)	O′(1)–N′(3)–O′(2)	121·5(6)
C′(1)–N′(1)–C′(2)	107·6(4)	O′(1)–N′(3)–N′(2)	123·0(6)
C′(2)–N′(1)–C′(2′)	113·2(4)	O′(2)–N′(3)–N′(2)	115·5(6)

(*g*) Intramolecular non-bonded distances (III)

O′(1) ··· N′(1)	2·65	O′(2) ··· N′(1)	3·50
O′(1) ··· C′(2)	2·85	N′(3) ··· C′(1)	3·55
O′(1) ··· H′(21)	2·26	N′(3) ··· C′(2)	2·95

TABLE 3 (*Continued*)

(*h*) Intermolecular distances (III)

$O'(1) \cdots O'(1^{I})$	3·37	$O'(2) \cdots C'(2^{III})$	3·44
$O'(1) \cdots N'(3^{I})$	3·65	$O'(2) \cdots C'(2^{I})$	3·62
$O'(1) \cdots C'(1^{II})$	3·02	$O'(2) \cdots C'(2^{IV})$	3·88
$O'(1) \cdots C'(2^{I})$	3·43	$N'(2) \cdots C'(1^{IV})$	3·69
$O'(2) \cdots N'(1^{III})$	3·67	$N'(2) \cdots C'(2^{IV})$	3·63
$O'(2) \cdots C'(1^{III})$	3·54	$N'(3) \cdots C'(1^{IV})$	3·72
$O'(2) \cdots C'(1^{IV})$	3·60	$N'(3) \cdots C'(2^{I})$	3·84

Roman numerals as superscripts refer to the equivalent positions which should be applied to the co-ordinates of the second atom:

I	$1 - x, \frac{1}{2} + y, 1 - z$	III	$x, y, -1 + z$
II	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$	IV	$\frac{1}{2} - x, -y, -\frac{1}{2} + z$

TABLE 4

Least-squares planes for (IIa)

(*a*) Atoms defining the planes

Plane (1): C(5)—(10)
Plane (2): O(1), N(2), C(4), C(5)
Plane (3): N(1), N(2), C(4)

(*b*) Plane equations

Plane (1): $0{\cdot}2586X' + 0{\cdot}7014Y' - 0{\cdot}6642Z' = 5{\cdot}2347$
Plane (2): $0{\cdot}0145X' + 0{\cdot}5667Y' - 0{\cdot}8238Z' = 3{\cdot}0936$
Plane (3): $0{\cdot}0345X' + 0{\cdot}5386Y' - 0{\cdot}8418Z' = 3{\cdot}1207$

(*c*) Deviation of atoms (Å) from planes

Plane (1): C(5) 0·010, C(6) −0·002, C(7) −0·005, C(8) 0·005, C(9) 0·003, C(10) −0·010, O(1) −0·124, N(2) 0·567, C(4) 0·141
Plane (2): O(1) 0·003, C(4) −0·009, N(2) 0·003, C(5) 0·002

(*d*) Dihedral angles (°) between planes

(1)–(2) 18·5, (2)–(3) 2·2

intra- and inter-molecular non-bonded distances; estimated standard deviations are derived from the inverses of the respective least-squares normal-equation matrices. For (IIa), the mean σ for C–O, C–N, C–C, and N–N bonds is 0·006 Å, for C–H bonds 0·05 Å, and for valency angles 0·4°. The corresponding values for (III) are 0·008 and 0·06 Å, and 0·5°. These are probably best regarded as minimum values, especially for (IIa) where the block-diagonal approximation was used in the final stages of the least-squares refinement.

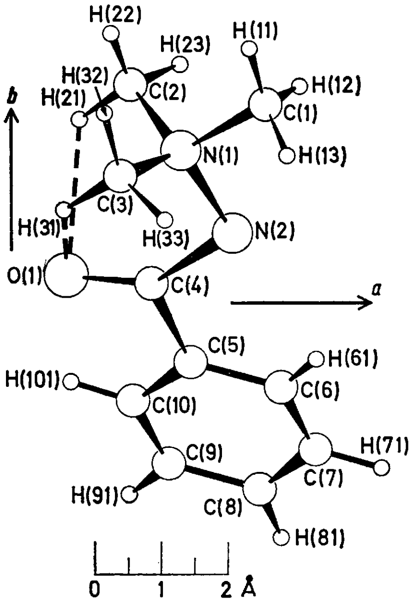


FIGURE 1 Molecule of (IIa) showing the atomic numbering

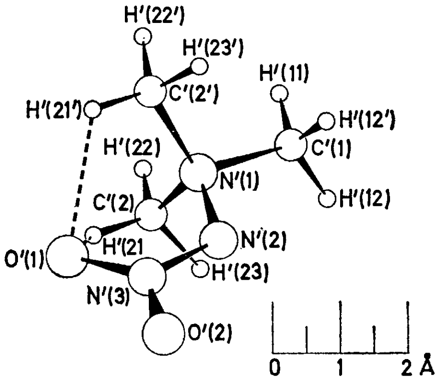


FIGURE 2 Molecule of (III) showing the atomic numbering. [Since the numbering has been chosen to correspond with that of (IIa), all atoms of (III) are shown with a prime]

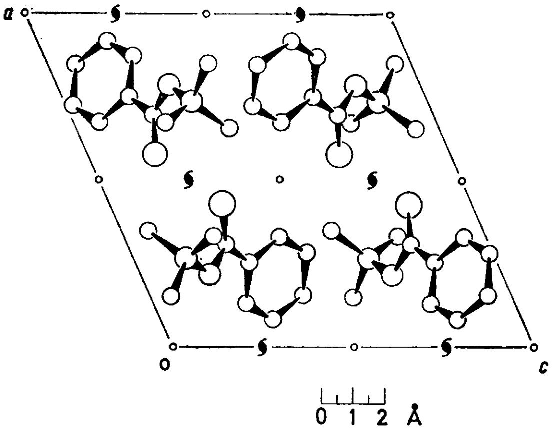


FIGURE 3 A projected view of the molecular packing of (IIa)

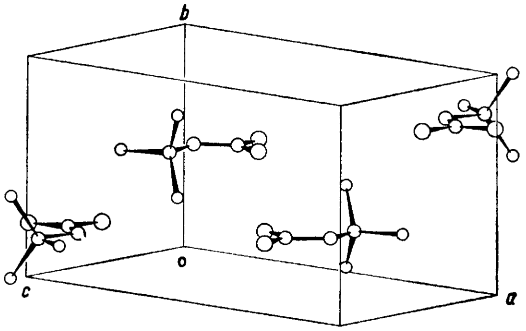


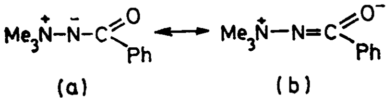
FIGURE 4 A view of the contents of one unit cell of (III)

Details of least-squares planes calculated for various portions of the molecular framework of (IIa) are given in Table 4. The atomic numbering schemes are shown in Figures 1 and 2; Figure 3 shows a projected view of the molecular packing of (IIa) and Figure 4 gives a three-dimensional view of the contents of a unit cell of (III).

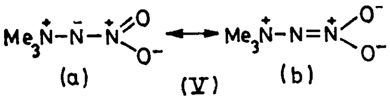
DISCUSSION

The structure analyses of the compounds (IIa) and (III) have not only revealed some interesting geometrical features of the class of ylides which they represent, but also allow comparisons to be made with the bonding and charge distributions found in the series of compounds (I; X = O, N$^-$, C<).

Examination of the relevant bond lengths in (IIa) and (III) shows that the N(1)–N(2) [1·471(5) Å] and N′(1)–N′(2) [1·470(8) Å] bonds are identical, within experimental error, and are similar to the N–N single-bond value of 1·45 Å found in hydrazine.[9] Since it has been demonstrated that opposite formal charges across a bond have a shortening effect,[10] the absence of any such shortening in the N(1)–N(2) and N′(1)–N′(2) bonds is consistent with minor contributions from the resonance forms (IVa) and (Va) respectively in which negative charges are placed on N(2) and N′(2), and is therefore also consistent with delocalisation of the negative charge into the respective electronegative moieties. Moreover, the N(2)–C(4) [1·313(6) Å] and N′(2)–N′(3) [1·323(8) Å] bonds are not much longer than the values of 1·27—1·29 Å [11] and 1·25 Å [9] quoted for C:N and N:N bonds respectively, but are appreciably shorter than the values of 1·47 Å [12] and 1·45 Å [9] given for corresponding single bonds. The lengths of the N(2)–C(4) and N′(2)–N′(3) bonds would therefore indicate important contributions from the canonical forms (IVb) and (Vb) in which there is significant charge delocalisation onto the carbonyl and nitro-oxygen atoms respectively. In accord with this suggestion, both the carbonyl bond of (IIa) [1·243(5) Å] and the nitro-bonds of (III) [mean 1·259(6) Å] are slightly longer than would be expected for similar bonds in environments where no charge delocalisation can take place. Moreover, it is usually found that significant delocalisation into such groups results in only slight lengthening of the oxygen bonds.

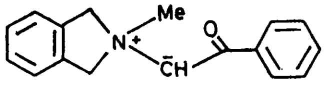


(IV)



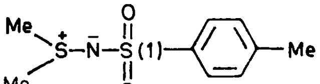
(V)

Analysis of the similar first-row ylide (VI),[13] in which the electronegative atom X is carbon, reveals that in this case the carbonyl bond is considerably lengthened (1·27 Å), while the adjacent C–C bond (1·36 Å) approaches a double-bond value. By comparing the dimensions of (VI) with the dimensions of (IIa) and (III), it is possible to contrast the bonding properties of first-row ylides of the type (I; X = O, N$^-$, C<). Since the amine oxides (I; X = O) are stable compounds, it must be concluded that the negative charge can reside on the oxygen atom without the need for further stabilisation. However, for nitrogen (I; X = N$^-$) and then carbon ylides (I; X = C<), increasing stabilisation is required in the form of increasing charge delocalisation into the attached electronegative groupings. This order of increasing charge delocalisation required by each system is that which would be expected on simple electronegativity grounds.

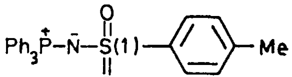


(VI)

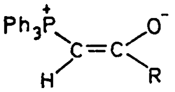
The solid-state conformations of (IIa) and (III) are almost identical, and are characterised by *syn*-planar relationships within the N(1)–N(2)–C(4)–O(1) and N′(1)–N′(2)–N′(3)–O′(1) systems respectively, the torsion angle about the N(2)–C(4) bond being *ca.* 2°, and that about the N(2′)–N(3′) bond being restricted to 0°. In (IIa) and (III) the *cis*-relationships may be regarded as arising, at least in part, from electrostatic interactions between the quaternary nitrogen atoms and the appropriate oxygen atoms; in (IIa) the N(1) · · · O(1) separation is 2·74 Å, and in (III) the N′(1) · · · O′(1) distance is 2·65 Å, both values being considerably smaller than the sum of the van der Waals' radii (*ca.* 2·90 Å). These similar conformations may be contrasted with that observed in the sulphonyl-stabilised sulphur–nitrogen (VII) [14] and phosphorus–nitrogen (VIII) [14] second-row ylides, in which d_π–p_π bonding is allowed. In both the last-named molecules, no such coplanarity is found for the corresponding group of atoms, the torsion angles about the N–S(1) bonds in (VII) and (VIII) being 36·8 and 37·6° respectively.



(VII)



(VIII)



(IX) R
a ; H
b ; Me
c ; OMe

By use of variable-temperature n.m.r. techniques, further information concerning the conformations of ylides has recently been gained from internal rotation measurements about carbon atoms α and β to the phosphorus in carbonyl-stabilised phosphoranes. It has

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been found that the formyl (IXa)[15] and acetyl (IXb)[15,16] derivatives exhibit no conformational mobility, existing as static conformers with the phosphorus usually *cis* to the oxygen. However, ester-stabilised systems exemplified by the methoxycarbonylphosphorane (IXc) rotate readily.[15a,17] We have carried out variable-temperature n.m.r. experiments on the compounds (II; a—d) with a view to determining the barriers to rotation around the N(2)–C(4) bond at temperatures between −80 and +110 °C. The ambient temperature spectra of (II; a—d) in $CDCl_3$ gave singlet resonances (Table 5) which are readily assigned. These spectra remain invariant † over the temperature range quoted, and provide no evidence for conformational mobility about the N(2)–C(4) bonds. It is possible, therefore, that (II; a—d) exist solely in a *cis*-conformation as revealed by the present *X*-ray studies. Moreover, although the n.m.r. spectra of ester-stabilised ylides of phosphorus,[15a,18] arsenic,[19] and sulphur,[15a] exhibit a temperature dependence which may be interpreted in terms of a *cis–trans* equilibrium associated with internal rotation about the enolate C–C bond, no such dependence could be obtained in the case of (IId). Investigations are, however, in hand with other ester groupings in an attempt to ascertain more definitively the conformational characteristics of ester-stabilised *N*-ammonioamidates.

TABLE 5

Chemical shift data * for compounds (II; a—d)

(IIa): 207·5 (9H, s), 443·5 (3H, br), 480·0 (2H, br)
(IIb): 461·8 [1H, s (br, $W_{\frac{1}{2}}$ 5·8 Hz)], 207·0 (9H, s)
(IIc): 206·1 (9H, s), 112·2 (3H, s)
(IId): 215·2 (9H, s), 204·2 (3H, s)

* Quoted in Hz downfield from tetramethylsilane and referred to solutions (10—15%, w/v) in deuteriochloroform. Spectra were recorded on a Varian HA 100 spectrometer with a probe temperature of 35°. Variable-temperature n.m.r. determinations were performed with 10—15% (w/v) solutions in deuteriochloroform, deuteriochloroform–carbon disulphide, or carbon disulphide. Spectra run at temperatures >60° were determined with pentachloroethane as solvent; a satisfactory temperature overlap with deuteriochloroform was executed.

A further feature of the conformations of (IIa) and (III) is that the N(1) and N′(1) substituents and the methyl hydrogen atoms are all fully staggered. A consequence of this and of the *cis*-conformations, is to place two methyl hydrogen atoms of each molecule in close proximity to the carbonyl oxygen of (IIa) and to one of the nitro-oxygen atoms of (III), the H · · · O separations being 2·17(5) and 2·27(5) in (IIa), and 2·26(5) Å in (III). The mean C–H · · · O angle in (IIa) is 123°, and in (III) is 120°. For significant interaction to exist between hydrogen and oxygen atoms, it has been stated that the H · · · O separation may not exceed 2·4 Å.[20] A possible interpretation, therefore, of the conformations and non-bonded separations of both (IIa) and (III), is that there exists a degree of hydrogen–oxygen interaction, although this can at best be very weak. However, it has not been possible to adduce any evidence for C–H · · · O hydrogen bonding by variable-temperature n.m.r. techniques using carbon disulphide solutions of (IIa).

With the exception of the valency angle O(1)–C(4)–N(2) [129·6(4)°] in (IIa), examination of the dimensions of the remainder of the molecules reveals no unexpected features. It is likely that the value for the O(1)–C(4)–N(2) angle reflects a degree of mutual repulsion between the N(2)–C(4) and C(4)–O(1) bonds, both of which have considerable double-bond character. The possibility of an extra repulsion effect by the two methyl groups involved in the weak C–H · · · O interaction may be partially discounted, since an angle of comparable magnitude [128·6°] has been observed recently for the amide grouping in a carbamoyl chloride.[21]

There are no short intermolecular contacts of significance in either structure, and it may be assumed, therefore, that the packing in both crystals has been determined by van der Waals' forces.

We thank the Carnegie Trust for the Universities of Scotland for a post-graduate award (to N. J. H.).

[2/203 *Received*, 1*st February*, 1972]

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† For (IIb) a temperature dependence was observed, but this is unconnected with rotational properties of the hetero-enolate moiety. At ambient temperature the formyl resonance H_a was broad $W_{\frac{1}{2}}$ 5·8 Hz; on lowering the temperature to −75 °C, significant sharpening of the signal occurred to give a singlet $W_{\frac{1}{2}}$ 1·9 Hz. This reversible phenomenon is in accord with expectations based on coupling between hydrogens and a nucleus with a quadrupole moment.[18] It is generally observed that such coupling occurs between ^{14}N (quaternised nitrogen in (IIb)) and a β-hydrogen. Above room temperature it is expected that the formyl proton will give a triplet resonance; in practice, however, irreversible thermal decomposition of the ylide set in at 105 °C, at which temperature no discernible sharpening to a triplet was apparent.

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