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The Structures of the Angular Dimers Formed by 2-Phenylbenzazete, 2-(*p*-Methoxyphenyl)benzazete and 2-(*tert*-Butyl)benzazete

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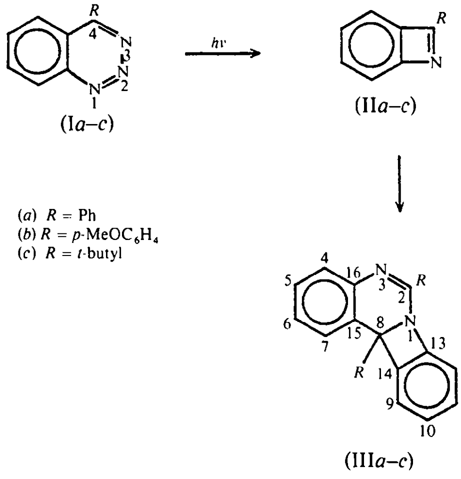
Abstract

The structures of the angular dimers (III*a*–*c*) formed by the title compounds have been determined by X-ray analysis (Mo $K\alpha$ radiation, λ = 0·7107 Å). (III*a*), $C_{26}H_{18}N_2$, M_r = 358·6, and (III*c*), $C_{22}H_{26}N_2$, M_r = 318·5, are triclinic, space group $P\bar{1}$, Z = 2, with a = 6·711 (1), b = 12·456 (2), c = 11·796 (2) Å, α = 87·0 (1), β = 78·2 (1), γ = 74·4 (1)°, U = 929·66 Å^3, D_c = 1·27 Mg m^{-3}, F(000) = 376, μ(Mo K) = 0·082 mm^{-1} for (III*a*), and a = 10·185 (1), b = 9·307 (1), c = 10·170 (1) Å, α = 91·8 (1), β = 94·9 (1), γ = 103·2 (1)°, U = 933·84 Å^3, D_c = 1·13 Mg m^{-3}, F(000) = 344, μ(Mo K) = 0·072 mm^{-1} for (III*c*). (III*b*), $C_{28}H_{22}N_2O_2$, M_r = 418·5, is monoclinic, space group $P2_1/c$, with Z = 4, a = 8·526 (1), b = 23·003 (3), c = 12·415 (1) Å, β = 112·5 (1)°, U = 2249·53 Å^3, D_c = 1·24 Mg m^{-3}, F(000) = 880, μ(Mo K) = 0·085 mm^{-1}. The three structures were solved by direct methods, quartets being used for (III*a*) and (III*c*). Refinements by least squares were terminated when R was 0·045, 0·043 and 0·060 for (III*a*–*c*) respectively (2114, 3184 and 3752 independent reflections). The analyses resolve ambiguities surrounding the structures of the angular dimers formed by the title compounds which were themselves formed by photolysis of the corresponding 4-substituted 1,2,3-benzotriazines (I*a*–*c*), and confirm that at least in the present cases, different substituents have not resulted in the production of the different isomeric forms possible for the dimers.

Introduction

Photolysis of the 4-aryl- and 4-alkyl-1,2,3-benzotriazines (I*a*–*c*) yielded the benzazetes (II*a*–*c*), which then dimerized to yield products thought to be (III*a*–*c*). However, the structures of the dimers (III*a*–*c*) were in doubt because of the difficulty of differentiating between the different possible regio-isomeric angular dimers, the nature of which could possibly have been influenced by different 4-substituents in the benzotriazines (I*a*–*c*). Analyses of (III*a*–*c*) confirm the structures shown, and reveal that at least in those cases studied, different 4-substituents in (I*a*–*c*) have not resulted in different regio-isomers of the angular dimers. In addition, confirmation of the structures (III*a*–*c*) indicates that the formation of these angular dimers may be the result of a Diels–Alder reaction, since the regioselectivity observed is that anticipated if the addition proceeds through a zwitterion or involves a transition state with appreciable polar character (Rees, Storr & Whittle, 1976; Rees, 1976).



(I*a*–*c*)

(II*a*–*c*)

(*a*) R = Ph
(*b*) R = *p*-MeOC$_6$H$_4$
(*c*) R = *t*-butyl

(III*a*–*c*)

Experimental

Crystallographic measurements

For all three compounds, initial cell parameters were determined photographically and refined by least squares prior to the data collections. Intensity measurements were made on a Hilger & Watts Y290 diffractometer with graphite-monochromated Mo radiation. 2114, 3184 and 3752 independent reflections with $I \geq 3\sigma_I$ were recorded by the θ,ω-scan technique in the ranges 2θ 0–60°, 0–54° and 0–60° for (III*a*–*c*) respectively. Intensities were corrected for Lorentz and polarization effects, but absorption was ignored.

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Structure determinations and refinements

(III*a*) and (III*c*) crystallize in space group $P\bar{1}$. Crystal structures in symmorphic space groups are traditionally the most difficult to solve *via* direct methods since the lack of translational symmetry tends to make the process ill-conditioned, and the lack of equivalent reflections can give rise to a paucity of sign relationships of high associated probability. Such factors force a need for a relatively large number of possible solutions from which the correct set may be difficult to extract. The strategy outlined below was therefore employed in the solutions of (III*a*) and (III*c*).

A set of quartet invariants was generated for the top 100 E magnitudes from the seven-magnitude, second-neighbourhood formula $P_7^{\pm}$ derived by Hauptman & Green (1976). These quartets were input into a modified version of *PHASE* (Stewart, 1970) in the XRAY system of Stewart, Kruger, Ammon, Dickinson & Hall (1972). In its standard form, this program attempts to produce a single set of phases for space groups having translational symmetry. In symmorphic cases a multisolution environment or the trivial all-plus situation is likely. Conventionally used, the program employs quartets derived *via* an overlap of two triplets.

Table 1. *Atomic parameters for* (III*a*) ($\times 10^4$ *for coordinates*, Å$^2 \times 10^3$ *for* U_{eq})

	x	y	z	U_{eq}*
N(1)	2381 (4)	7467 (2)	7003 (2)	32 (2)
C(2)	2061 (5)	6684 (3)	7864 (3)	32 (2)
N(3)	2731 (4)	6628 (2)	8819 (2)	37 (2)
C(4)	5276 (6)	6972 (3)	9824 (3)	45 (2)
C(5)	6726 (6)	7531 (4)	9967 (4)	52 (2)
C(6)	7116 (6)	8363 (4)	9212 (4)	56 (2)
C(7)	6054 (6)	8647 (3)	8300 (3)	47 (2)
C(8)	3324 (5)	8417 (2)	7209 (3)	33 (2)
C(9)	6058 (6)	8436 (3)	5083 (3)	45 (2)
C(10)	6643 (7)	7745 (4)	4093 (3)	49 (2)
C(11)	5757 (6)	6869 (3)	4026 (3)	46 (2)
C(12)	4227 (6)	6609 (3)	4922 (3)	41 (2)
C(13)	3719 (5)	7292 (3)	5877 (3)	33 (2)
C(14)	4594 (5)	8169 (3)	5961 (3)	34 (2)
C(15)	4565 (5)	8105 (3)	8156 (3)	34 (2)
C(16)	4164 (5)	7254 (3)	8918 (3)	35 (2)
C(21)	787 (5)	5942 (2)	7655 (3)	32 (2)
C(22)	596 (6)	5054 (3)	8410 (3)	40 (2)
C(23)	−667 (6)	4383 (3)	8256 (4)	51 (2)
C(24)	−1702 (7)	4560 (3)	7334 (4)	60 (2)
C(25)	−1501 (7)	5421 (3)	6574 (4)	59 (2)
C(26)	−285 (6)	6122 (3)	6740 (3)	44 (2)
C(81)	1609 (5)	9511 (2)	7394 (3)	33 (2)
C(82)	326 (6)	9852 (3)	6578 (3)	39 (2)
C(83)	−1331 (6)	10815 (3)	6739 (4)	48 (2)
C(84)	−1729 (7)	11441 (3)	7729 (4)	47 (2)
C(85)	−472 (7)	11125 (3)	8537 (4)	50 (2)
C(86)	1204 (6)	10160 (3)	8378 (3)	43 (2)

* In this and subsequent tables, U_{eq} is defined to be $(U_1 . U_2 . U_3)^{1/3}$.

Table 2. *Atomic parameters for* (III*b*) ($\times 10^4$ *for coordinates*, Å$^2 \times 10^3$ *for* U_{eq})

	x	y	z	U_{eq}
N(1)	5204 (3)	1407 (1)	2025 (1)	35 (1)
C(2)	4996 (2)	1054 (1)	2870 (2)	34 (1)
N(3)	3928 (2)	1162 (1)	3354 (1)	45 (1)
C(4)	1276 (4)	1591 (1)	3177 (2)	54 (1)
C(5)	−82 (4)	1961 (1)	2636 (2)	57 (1)
C(6)	−80 (4)	2330 (1)	1762 (2)	49 (1)
C(7)	1285 (4)	2332 (1)	1415 (2)	43 (1)
C(8)	4180 (2)	1984 (1)	1603 (2)	34 (1)
C(9)	3188 (4)	1846 (1)	−811 (2)	42 (1)
C(10)	3445 (4)	1407 (1)	−1504 (2)	48 (1)
C(11)	4358 (3)	907 (1)	−1035 (2)	52 (1)
C(12)	5095 (4)	808 (1)	170 (2)	46 (1)
C(13)	4825 (2)	1246 (1)	828 (2)	37 (1)
C(14)	3911 (2)	1746 (1)	370 (2)	38 (1)
C(15)	2654 (2)	1962 (1)	1940 (2)	36 (1)
C(16)	2649 (2)	1582 (1)	2821 (2)	39 (1)
C(21)	6113 (2)	541 (1)	3225 (1)	35 (1)
C(22)	7603 (2)	493 (1)	3015 (2)	39 (1)
C(23)	8639 (2)	9 (1)	3376 (2)	42 (1)
C(24)	8203 (2)	−434 (1)	3967 (1)	36 (1)
O(24)	9110 (3)	−930 (1)	4364 (1)	48 (1)
C(241)	10587 (4)	−1018 (1)	4110 (2)	56 (1)
C(25)	6725 (2)	−389 (1)	4191 (2)	42 (1)
C(26)	5685 (2)	87 (1)	3813 (2)	42 (1)
C(81)	5267 (2)	2500 (1)	2027 (2)	37 (1)
C(82)	6285 (3)	2560 (1)	3203 (2)	41 (1)
C(83)	7281 (4)	3049 (1)	3621 (2)	52 (1)
C(84)	7249 (4)	3491 (1)	2859 (2)	52 (1)
O(84)	8151 (2)	3999 (1)	3180 (2)	75 (1)
C(841)	9299 (7)	4059 (2)	4362 (4)	98 (1)
C(85)	6239 (4)	3440 (1)	1686 (2)	53 (1)
C(86)	5262 (2)	2946 (1)	1272 (2)	45 (1)

Table 3. *Atomic parameters for* (III*c*) ($\times 10^4$ *for coordinates*, Å$^2 \times 10^3$ *for* U_{eq})

	x	y	z	U_{eq}
N(1)	2248 (3)	3677 (2)	8889 (2)	39 (2)
C(2)	2860 (2)	2818 (2)	9707 (2)	40 (2)
N(3)	3511 (2)	1897 (2)	9256 (2)	48 (2)
C(4)	4902 (2)	1369 (3)	7601 (3)	59 (2)
C(5)	5367 (3)	1545 (4)	6372 (3)	71 (2)
C(6)	4847 (3)	2385 (4)	5486 (3)	71 (2)
C(7)	3824 (3)	3057 (3)	5800 (2)	58 (2)
C(8)	2121 (2)	3450 (2)	7397 (2)	39 (2)
C(9)	2353 (2)	6333 (3)	6637 (2)	56 (2)
C(10)	2580 (3)	7699 (3)	7346 (3)	62 (2)
C(11)	2712 (3)	7800 (3)	8703 (2)	61 (2)
C(12)	2630 (3)	6565 (3)	9474 (3)	54 (2)
C(13)	2430 (2)	5248 (2)	8760 (2)	42 (2)
C(14)	2294 (2)	5135 (2)	7388 (2)	43 (2)
C(15)	3297 (2)	2846 (2)	7014 (2)	42 (2)
C(16)	3863 (2)	2039 (2)	7942 (2)	44 (2)
C(21)	2710 (2)	2922 (3)	11182 (2)	49 (2)
C(211)	1319 (2)	3173 (4)	11418 (3)	77 (2)
C(212)	2883 (4)	1505 (4)	11805 (4)	75 (2)
C(213)	3847 (2)	4200 (4)	11806 (3)	73 (2)
C(81)	701 (2)	2509 (2)	6846 (2)	49 (2)
C(811)	554 (3)	2587 (4)	5343 (3)	73 (2)
C(812)	544 (3)	921 (3)	7226 (4)	66 (2)
C(813)	−404 (3)	3135 (4)	7411 (4)	68 (2)

Table 4. *Bond distances* (Å) *and angles* (°) *for* (III*a–c*)

(*a*) Bond distances

	(III*a*)	(III*b*)	(III*c*)
N(1)–C(2)	1·396 (4)	1·391 (2)	1·379 (3)
N(1)–C(8)	1·535 (4)	1·526 (2)	1·516 (3)
N(1)–C(13)	1·434 (4)	1·443 (2)	1·443 (2)
C(2)–N(3)	1·288 (4)	1·293 (2)	1·293 (3)
C(2)–C(21)	1·477 (4)	1·474 (2)	1·523 (3)
N(3)–C(16)	1·416 (4)	1·417 (2)	1·415 (3)
C(4)–C(5)	1·380 (5)	1·386 (3)	1·375 (4)
C(4)–C(16)	1·403 (5)	1·401 (3)	1·407 (3)
C(5)–C(6)	1·375 (6)	1·378 (3)	1·362 (4)
C(6)–C(7)	1·389 (6)	1·387 (3)	1·386 (4)
C(7)–C(15)	1·388 (5)	1·389 (3)	1·390 (3)
C(8)–C(14)	1·543 (4)	1·542 (2)	1·538 (3)
C(8)–C(15)	1·501 (4)	1·511 (2)	1·509 (3)
C(8)–C(81)	1·521 (4)	1·511 (2)	1·557 (3)
C(9)–C(10)	1·412 (5)	1·397 (3)	1·403 (4)
C(9)–C(14)	1·368 (5)	1·375 (2)	1·364 (3)
C(10)–C(11)	1·388 (6)	1·386 (3)	1·373 (5)
C(11)–C(12)	1·405 (5)	1·402 (3)	1·402 (4)
C(12)–C(13)	1·377 (5)	1·371 (3)	1·370 (3)
C(13)–C(14)	1·389 (4)	1·384 (3)	1·389 (3)
C(15)–C(16)	1·400 (5)	1·401 (2)	1·392 (3)
C(21)–C(22)	1·400 (5)	1·396 (2)	
C(21)–C(26)	1·392 (5)	1·400 (2)	
C(22)–C(23)	1·382 (5)	1·385 (3)	
C(23)–C(24)	1·384 (3)	1·387 (2)	
C(24)–C(25)	1·378 (6)	1·394 (2)	
C(25)–C(26)	1·390 (6)	1·374 (2)	
C(81)–C(82)	1·396 (5)	1·391 (2)	
C(81)–C(86)	1·388 (5)	1·389 (2)	
C(82)–C(83)	1·390 (5)	1·385 (3)	
C(83)–C(84)	1·378 (5)	1·382 (3)	
C(84)–C(85)	1·373 (6)	1·384 (3)	
C(85)–C(86)	1·398 (5)	1·386 (3)	
C(24)–O(24)		1·361 (2)	
O(24)–C(241)		1·425 (3)	
C(84)–O(84)		1·372 (3)	
O(84)–C(841)		1·425 (5)	
C(21)–C(211)			1·525 (4)
C(21)–C(212)			1·520 (4)
C(21)–C(213)			1·535 (4)
C(81)–C(811)			1·529 (4)
C(81)–C(812)			1·516 (4)
C(81)–C(813)			1·525 (4)
Mean C–H	1·035	0·914	0·975

(*b*) Bond angles

	(III*a*)	(III*b*)	(III*c*)
C(8)–N(1)–C(2)	121·1 (2)	121·9 (1)	122·1 (2)
C(13)–N(1)–C(2)	128·7 (3)	125·7 (1)	134·1 (2)
C(13)–N(1)–C(8)	89·4 (2)	89·4 (1)	89·7 (1)
N(3)–C(2)–N(1)	123·2 (3)	123·7 (2)	122·1 (2)
C(21)–C(2)–N(1)	116·2 (3)	116·0 (2)	118·4 (2)
C(21)–C(2)–N(3)	120·6 (3)	120·3 (2)	119·4 (2)
C(16)–N(3)–C(2)	118·3 (3)	117·8 (2)	117·4 (2)
C(16)–C(4)–C(5)	120·5 (4)	120·0 (2)	119·9 (2)
C(6)–C(5)–C(4)	120·2 (4)	120·5 (2)	120·6 (3)
C(7)–C(6)–C(5)	120·3 (4)	120·0 (2)	120·5 (3)
C(15)–C(7)–C(6)	120·2 (4)	120·4 (2)	120·0 (2)
C(14)–C(8)–N(1)	84·9 (2)	85·3 (1)	85·4 (1)
C(15)–C(8)–N(1)	110·0 (2)	110·0 (1)	108·3 (2)
C(15)–C(8)–C(14)	116·0 (3)	117·2 (1)	116·8 (2)
C(81)–C(8)–N(1)	110·2 (3)	111·8 (1)	112·1 (2)
C(81)–C(8)–C(14)	116·3 (3)	116·7 (1)	115·6 (2)
C(81)–C(8)–C(15)	115·1 (3)	112·6 (1)	114·6 (2)
C(14)–C(9)–C(10)	115·3 (3)	115·1 (3)	115·4 (2)
C(11)–C(10)–C(9)	121·6 (4)	122·4 (2)	121·6 (3)
C(12)–C(11)–C(10)	123·0 (4)	122·2 (2)	123·0 (2)
C(13)–C(12)–C(11)	113·7 (3)	114·1 (2)	114·4 (2)
C(12)–C(13)–N(1)	141·0 (3)	141·2 (2)	143·0 (2)
C(14)–C(13)–C(12)	124·1 (3)	124·2 (2)	123·1 (2)
C(14)–C(13)–N(1)	94·9 (3)	94·5 (1)	94·0 (2)
C(9)–C(14)–C(8)	146·9 (3)	147·1 (2)	146·5 (2)
C(13)–C(14)–C(8)	90·7 (3)	90·9 (1)	90·9 (2)
C(13)–C(14)–C(9)	122·4 (3)	122·0 (2)	122·6 (2)
C(15)–C(16)–N(3)	124·1 (3)	123·9 (2)	124·2 (2)
C(4)–C(16)–N(3)	117·1 (3)	116·7 (2)	116·4 (2)
C(15)–C(16)–C(4)	118·8 (3)	119·3 (2)	119·3 (2)
C(8)–C(15)–C(7)	121·8 (2)	121·7 (2)	123·4 (3)
C(16)–C(15)–C(7)	119·9 (3)	119·7 (2)	119·6 (2)
C(16)–C(15)–C(8)	118·2 (3)	118·6 (2)	117·0 (2)
C(22)–C(21)–C(2)	119·6 (3)	122·5 (2)	
C(26)–C(21)–C(2)	121·5 (3)	119·0 (2)	
C(26)–C(21)–C(22)	118·9 (3)	118·4 (2)	
C(23)–C(22)–C(21)	120·2 (3)	121·1 (2)	
C(24)–C(23)–C(22)	120·4 (4)	119·7 (2)	
C(25)–C(24)–C(23)	119·9 (4)	119·8 (2)	
C(26)–C(25)–C(24)	120·2 (4)	120·4 (2)	
C(21)–C(26)–C(25)	120·4 (3)	120·6 (2)	
C(82)–C(81)–C(8)	119·2 (3)	120·0 (2)	
C(86)–C(81)–C(8)	122·2 (3)	121·7 (2)	
C(86)–C(81)–C(82)	118·5 (3)	118·3 (2)	
C(84)–C(83)–C(82)	119·4 (4)	119·5 (2)	
C(83)–C(82)–C(81)	121·3 (3)	121·4 (2)	
C(85)–C(84)–C(83)	120·1 (4)	119·9 (2)	
C(86)–C(85)–C(84)	120·8 (4)	120·2 (2)	
C(85)–C(86)–C(81)	119·9 (3)	120·6 (2)	
C(23)–C(24)–O(24)		125·3 (2)	
C(25)–C(24)–O(24)		114·9 (2)	
C(24)–O(24)–C(241)		117·8 (2)	
C(83)–C(84)–O(84)		124·5 (2)	
C(85)–C(84)–O(84)		115·6 (2)	
C(84)–O(84)–C(841)		118·0 (2)	
C(211)–C(21)–C(2)			110·4 (2)
C(212)–C(21)–C(2)			110·0 (2)
C(213)–C(21)–C(2)			107·6 (2)
C(211)–C(21)–C(212)			109·2 (2)
C(211)–C(21)–C(213)			111·2 (2)
C(212)–C(21)–C(213)			108·3 (2)
C(811)–C(81)–C(8)			108·8 (2)
C(812)–C(81)–C(8)			110·2 (2)
C(813)–C(81)–C(8)			109·8 (2)
C(811)–C(81)–C(812)			110·5 (3)
C(811)–C(81)–C(813)			108·6 (2)
C(812)–C(81)–C(813)			109·0 (2)

(*c*) Selected torsion angles. Mean e.s.d.'s are 0·4° for (III*a*) and 0·2° for (III*b*) and (III*c*).

	(III*a*)	(III*b*)	(III*c*)
C(8)–N(1)–C(2)–N(3)	−7·8	0·7	8·9
N(1)–C(2)–N(3)–C(16)	−11·4	14·7	14·9
C(2)–N(3)–C(16)–C(15)	14·1	−12·4	−15·9
N(3)–C(16)–C(15)–C(8)	3·2	−5·5	−7·5
C(16)–C(15)–C(8)–N(1)	−19·7	18·4	27·1
C(15)–C(8)–N(1)–C(2)	22·8	−17·1	−29·4
C(13)–N(1)–C(8)–C(14)	2·3	−1·3	−1·1
N(1)–C(8)–C(14)–C(13)	−2·4	1·4	1·2
C(8)–C(14)–C(13)–N(1)	2·6	−1·4	−1·2
C(14)–C(13)–N(1)–C(8)	−2·6	1·5	1·3
C(13)–N(1)–C(2)–C(21)	−73·3	66·6	64·4
C(16)–N(3)–C(2)–C(21)	172·1	−166·9	−167·6
C(8)–N(1)–C(2)–C(21)	168·9	−177·8	−168·6
C(13)–C(14)–C(8)–C(81)	−112·4	113·4	113·6
C(7)–C(15)–C(8)–C(81)	−73·5	71·8	81·1
C(16)–C(15)–C(8)–C(81)	105·5	−107·1	−98·9
C(2)–N(1)–C(8)–C(81)	−105·2	108·9	98·0
C(13)–N(1)–C(8)–C(81)	118·5	−118·1	−117·1

Thus if:

$$\varphi_1 = \varphi_h + \varphi_k + \varphi_{h-k} \tag{1}$$

and

$$\varphi_2 = \varphi_l + \varphi_m + \varphi_{h+k} \tag{2}$$

where $h + k + l + m = 0$, addition of (1) and (2) gives:

$$\Phi_4 = \varphi_1 + \varphi_2 = \varphi_h + \varphi_k + \varphi_l + \varphi_m.$$

Since all the associated E magnitudes are large, all such quartets in symmorphic space groups will have $\Phi_4 = 0$, and the problems discussed previously still remain. However, it is a simple task to adapt *PHASE* to use quartets generated *via* the P_7^+ formula. The presence of negative quartets ($\Phi_4 = \pi$) alleviates the lack of translational symmetry and there is a large increase in the number of available phase relationships of high reliability (albeit these are interdependent).

For (III*a*) and (III*c*) this procedure was used to phase the top 100 E magnitudes, and in both cases only a single phase set was produced. The phases thus derived were expanded *via* routine application of triplet phase relationships to phase 242 $|E_{\mathbf{h}}| \geq 1{\cdot}8$ for (III*a*) and 236 $|E_{\mathbf{h}}| \geq 1{\cdot}8$ for (III*c*). The resulting E maps revealed the positions of all non-hydrogen atoms. Routine application of the unmodified version of *PHASE* failed to produce a unique solution in either case.

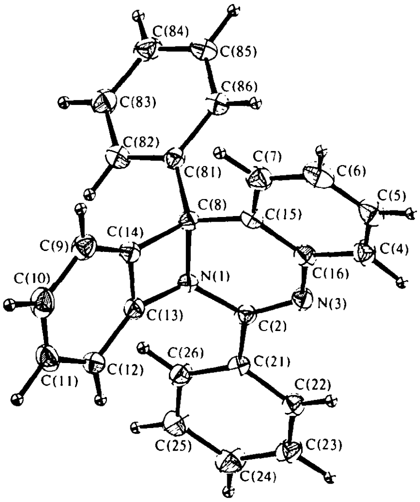

Fig. 1. A view of dimer (III*a*) with the atom numbering.

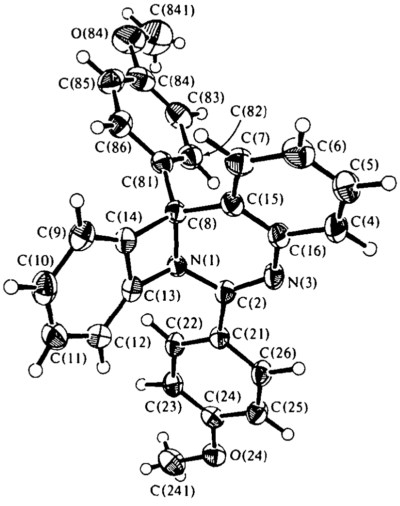

Fig. 2. A view of dimer (III*b*) with the atom numbering.

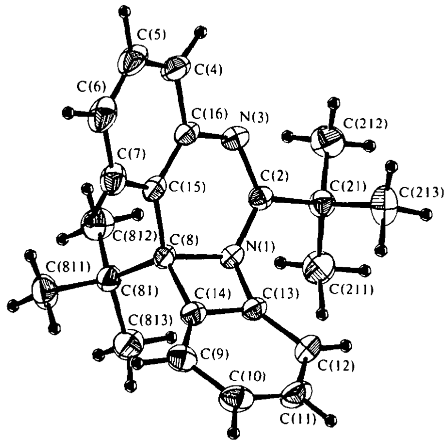

Fig. 3. A view of dimer (III*c*) with the atom numbering.

(III*b*) crystallizes in space group $P2_1/c$, and was solved by routine application of *PHASE*.

In all three cases the H atoms were located from a difference synthesis. The non-hydrogen atoms were refined with anisotropic thermal parameters with *CRYLSQ*. The H atom coordinates and thermal parameters were refined, except for (III*c*), where the temperature factors were fixed at $U = 0{\cdot}04$ Å^2. A polynomial weighting scheme was employed. At convergence R was 0·045, 0·043 and 0·060 for (III*a*–*c*) respectively ($R_w = 0{\cdot}05, 0{\cdot}061, 0{\cdot}057$). Tables 1, 2 and 3 give the atomic coordinates for (III*a*–*c*) respectively, while Table 4 summarizes, comparatively, bond distances, interbond angles and torsion angles for the three dimers. Figs. 1, 2 and 3 show *ORTEP* drawings for each molecule.*

Discussion of molecular geometries

The molecular geometries of (III*a*–*c*) are unremarkable and present no features of novel interest. We therefore confine ourselves to brief mention of a few salient points.

Comparable bond lengths for all three molecules are experimentally identical, with C(2)—N(3) virtually localized. Bond angles are also virtually identical, with the exception of C(13)—N(1)—C(2) in (III*c*), which is 134·1 (2)° in contrast to the 128·7 (3) and 125·7 (1)° in (III*a*) and (III*b*) respectively. This seems to reflect the different degrees of pyramidal nature of N(1) in the three molecules, rather than distortion of other interbond angles. Thus, N(1) in (III*c*) is the least pyramidal

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35977 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[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.

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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

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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-

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

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