86. Crystal Structure of (*Z*)-1-Phenyl- and of (*Z*)-1-Dimethylamino-2-phthalimido-diazene-1-oxide

by **Lienhard Hoesch**[1]) and **Jost H. Bieri**
Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

and **Jean Paul Declercq, Gabriel Germain** and **Maurice van Meerssche**
Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Place L. Pasteur, 1,
B-1348 Louvain-la-Neuve, Belgium

(21.XI.80)

Kristallstruktur von (*Z*)-1-Phenyl- und von (*Z*)-1-Dimethylamino-2-phthalimido-diazen-1-oxid

Zusammenfassung

Durch *Röntgen*-Strukturanalyse wurden die Konstitution und die (*Z*)-Konfiguration der im Titel genannten Produkte (**3a** und **3b**) aus der Addition von Phthalimido-nitren (**1**) an Nitrosobenzol (**2a**) bzw. an Dimethylnitrosamin (**2b**) im Einklang mit früheren, spektroskopischen Strukturzuordnungen bestätigt. In beiden Molekeln (**3a** und **3b**) ist die Phthalimidogruppe nicht mit der Diazenoxidfunktion konjugiert, dagegen besteht offensichtliche Konjugation der zentralen NNO-Funktion mit der Phenylgruppe in **3a** bzw. mit der Dimethylaminogruppe in **3b**. Die Ebene der NNO-Gruppe ist in beiden Molekeln nur wenig gegenüber derjenigen der Substituenten an N(1) verdrillt (5° bei **3a** bzw. 7° bei **3b**). Die Bindungslänge zwischen N(1) und dem Dimethylamino-Stickstoffatom in **3b** entspricht mit 1,347 Å nahezu einer N,N-Anderthalb-Bindung, und beide zuletzt genannten N-Atome sind coplanar mit ihren jeweiligen drei Liganden. Die Bindungslänge zwischen N(1) und dem benachbarten C-Atom in **3a** von 1,459 Å entspricht derjenigen einer Einfachbindung zwischen sp^2-hybridisierten N- bzw. C-Atomen, analog den Bindungslängen zwischen N(1) und dem benachbarten C-Atom in 1,2-Diaryl-diazen-1-oxiden (**5**; R, R' = Aryl).

---

1. Introduction. - Phthalimido-nitrene (**1**) forms (1:1)-adducts with *C*- and *N*-nitroso compounds (**2**, R = aryl, alkyl or amino) to which the constitution of 1-aryl-, 1-alkyl- and 1-amino-2-phthalimido-diazene-1-oxides (**3**, R = aryl, alkyl and amino, respectively) was assigned on the basis of their spectroscopic and chemical properties [1] [2]. Furthermore, for the aryl and alkyl substituted adducts **3** (R = aryl or alkyl) the (*Z*)-configuration with respect to the N(1),N(2)-bond was

---

[1]) Author to whom correspondence should be addressed. Present address: Institut für Pflanzenbiologie der Universität Zürich, Zollikerstrasse 107, CH-8008 Zürich.

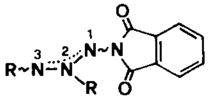
0018-019X/81/3/0905-10$01.00/0

1 **2** **a** $R = C_6H_5$ **3**
b $R = N(CH_3)_2$

deduced from their UV.- and ^{1}H-NMR.-spectra, whereas for the amino substituted adducts **3** (R = amino) no safe configurational assignment was possible.

In order to ensure the constitutional and configurational assignments for **3** (R = aryl, alkyl or amino) X-ray analyses were performed with crystals of the phenyl substituted adduct **3a** [1] and of the dimethylamino substituted adduct **3b** [2]. The results of these X-ray analyses are reported here.

We were interested moreover in bonding features and conformational properties of **3** to be deduced from the structural parameters of **3a** and **3b**, and to compare them with those of the 1-phthalimido-azimines **4**[2]) [3], and of the other diazene-oxides **5** [4] [5].



4

	R	Configuration N(2),N(3)
a	CH_3	*Z*
b	CH_3	*E*

5

	R	R′
a	C_6H_5	*p*-$CH_3C_6H_4$
	(*E*)-configuration	

2. X-ray analysis of 3a and 3b. - (*Z*)-1-Phenyl-2-phthalimido-diazene-1-oxide (**3a**), $C_{14}H_9N_3O_3$, $M = 267.25$, crystallized from hexane/dichloromethane in form of colourless needles, m.p. 160-162° (decomp.). (*Z*)-1-Dimethylamino-2-phthalimido-diazene-1-oxide (**3b**), $C_{10}H_{10}N_4O_3$, $M = 234.22$, crystallized from the same solvent system in form of colourless prismatic crystals, m.p. 170-172° (decomp.). *Table 1* summarizes the crystallographic data of **3a** and **3b**.

Diffraction data were collected with monochromatized MoK_α radiation on a *Syntex* $P2_1$ automatic fourcircle diffractometer. The intensities were collected from a crystal at *ca.* 18° to a resolution of 47° (2θ) utilizing the ω-scan technique.

Structure determination. A reflection was classified as observed with $I \geq 2.2\,\sigma(I)$. Initial models for the structures were obtained by direct methods. In the least square refinement all C-, N- and O-Atoms were refined anisotropically. The H-atoms of **3a** were calculated and kept fix during the last cycles while those of **3b** were located in a difference *Fourier* map and varied isotropically. The computer programs used were MULTAN 78 [6] and SHELX 76 [7].

Tables 2 and *3* list the computed atom coordinates with standard deviations. *Figure 1* shows stereopair views of **3a** and **3b** and *Figure 2* gives the numbering of atoms in **3a** and **3b** with bond lengths and some selected bond angles[3]). A complete list of structure factors and atomic parameters can be obtained from author (*J. H. B.*).

---

[2]) For **3a**, a pair of different neighbouring molecules is shown (*i.e.* **3a** and **3a′**); but the two molecules are identical with respect to bond lengths and bond angles within the standard deviations.

Table 1. *Crystallographic Data*

	3a	**3b**
Crystal system	orthorhombic	triclinic
Space group	$Pb2_1a$	$P\bar{1}$
Lattice parameters	a = 27.737 (12) Å b = 11.515 (6) Å c = 7.751 (2) Å	a = 8.726 (4) Å b = 7.920 (5) Å c = 7.941 (4) Å α = 101.41 (5)° β = 92.21 (4)° γ = 88.01 (4)°
Number of molecules per unit cell	8	2
Number of intensities		
measured	1939	1581
observed	1258	1359
R	0.054	0.037

Table 2. *Atomic coordinates* × 10^4 *for C-, N-, O- and H-atoms with e.s.d.'s. of* **3a** *and* **3a**'2)

Atom	x	y	z
N(1)	6761 (2)	3915 (10)	1665 (10)
N(2)	6503 (2)	3133 (9)	975 (9)
N(3)	6016 (2)	3386 (1)	1125 (9)
C(4)	5693 (2)	2519 (12)	1695 (13)
C(5)	5206 (3)	3020 (10)	1378 (11)
C(6)	4758 (3)	2571 (10)	1795 (11)
C(7)	4358 (3)	3212 (11)	1269 (13)
C(8)	4408 (3)	4223 (11)	366 (12)
C(9)	4851 (3)	4682 (11)	−74 (12)
C(10)	5254 (3)	4046 (10)	473 (11)
C(11)	5782 (3)	4289 (10)	231 (12)
O(12)	5975 (2)	5038 (9)	−593 (9)
O(13)	5809 (2)	1588 (9)	2296 (8)
O(14)	6605 (2)	4797 (10)	2373 (10)
C(15)	7281 (3)	3735 (10)	1620 (12)
C(16)	7567 (3)	4606 (11)	2265 (12)
C(17)	8069 (3)	4454 (12)	2274 (13)
C(18)	8257 (4)	3421 (12)	1639 (12)
C(19)	7971 (3)	2553 (11)	1013 (13)
C(20)	7470 (3)	2716 (11)	960 (11)
H–C(6)	4723 (3)	1767 (10)	2501 (11)
H–C(7)	4001 (3)	2900 (11)	1580 (13)
H–C(8)	4084 (3)	4677 (11)	−16 (12)
H–C(9)	4886 (3)	5481 (11)	−795 (12)
H–C(16)	7402 (3)	5379 (11)	2788 (12)
H–C(17)	8301 (3)	5141 (12)	2731 (13)
H–C(18)	8643 (4)	3294 (12)	1671 (12)
H–C(19)	8128 (3)	1753 (11)	549 (13)
H–C(20)	7234 (3)	2067 (11)	412 (11)
N(1')	3336 (3)	6466 (10)	3922 (11)

Table 2 (continued)

Atom	x	y	z
N(2′)	3554 (3)	5579 (10)	3576 (12)
N(3′)	4059 (2)	5745 (8)	3975 (9)
C(4′)	4366 (3)	6536 (11)	3182 (12)
C(5′)	4853 (3)	6186 (9)	3731 (11)
C(6′)	5299 (3)	6635 (11)	3310 (11)
C(7′)	5704 (3)	6076 (10)	3940 (13)
C(8′)	5666 (3)	5058 (11)	4951 (12)
C(9′)	5211 (3)	4621 (11)	5352 (12)
C(10′)	4812 (3)	5195 (11)	4716 (11)
C(11′)	4294 (3)	4864 (11)	4886 (14)
O(12′)	4104 (2)	4054 (9)	5597 (9)
O(13′)	4245 (2)	7313 (9)	2224 (9)
O(14′)	3475 (3)	7431 (10)	4561 (11)
C(15′)	2789 (3)	6406 (12)	3624 (13)
C(16′)	2510 (4)	7300 (12)	4171 (12)
C(17′)	2018 (3)	7201 (12)	3947 (13)
C(18′)	1824 (4)	6228 (12)	3164 (13)
C(19′)	2109 (4)	5334 (12)	2609 (14)
C(20′)	2612 (4)	5433 (13)	2827 (14)
H−C(6′)	5332 (3)	7403 (11)	2518 (11)
H−C(7′)	6058 (3)	6414 (10)	3655 (13)
H−C(8′)	5987 (3)	4612 (11)	5378 (12)
H−C(9′)	5172 (3)	3870 (11)	6173 (12)
H−C(16′)	2671 (4)	8041 (12)	4803 (12)
H−C(17′)	1785 (3)	7907 (12)	4329 (13)
H−C(18′)	1437 (4)	6160 (12)	3018 (13)
H−C(19′)	1950 (4)	4582 (12)	2001 (14)
H−C(20′)	2854 (4)	4758 (13)	2394 (14)

3. Discussion. - The X-ray analyses of the adducts of phthalimido-nitrene (**1**) to the nitroso compounds **2a** and **2b** confirm the previous constitutional assignments of **3a** and **3b**, respectively [1] [2]. In both cases the adducts have been formed by connecting the nitrene N-atom with the N-atom of the nitroso function in **2**, thereby generating an 1,3-dipolar NNO-grouping as in **6** ($X=O$; $R'=C_6H_5$ and $N(CH_3)_2$, respectively; R''=phthalimido). This follows from the fact that the new N(2),N(3)-bond as well as the N,O-bond have partial double bond character (see *Table 5*), and those atoms of the substituents R' and R'' which are bonded directly to the NNO-grouping lie in a common plane with N(1), N(2), and O(14) (for **3a**: C(15), for **3b**: N(15), and in both cases N(3)) (for numbering see *Fig. 2*). Furthermore, the X-ray analyses prove the (*Z*)-configuration for **3a** and **3b**.

In addition to the plane of the NNO-grouping (plane 1) in both molecules, two other planes of neighbouring atoms are present: (1) the plane of the phthalimido group (plane 2) covering the atoms N(3) and C(4) to C(11) in **3a** and **3b**. In the amino-substituted **3b** this plane includes also O(12), O(13) and N(2), whereas in **3a** the atoms N(3), C(4) and C(11) show significant out-of-plane deformations to bring N(2), O(12) and O(13) out of the phthalimido plane by

Table 3. *Atomic coordinates* × 10^4 *for C-, N-, O- and H-atoms with e.s.d.'s. of* **3b**

Atom	x	y	z
N(1)	8218 (2)	10227 (2)	8100 (2)
N(2)	7042 (2)	10263 (2)	9071 (2)
N(3)	6025 (2)	9015 (2)	8254 (2)
C(4)	6089 (2)	7289 (3)	8413 (3)
C(5)	4746 (2)	6515 (2)	7412 (2)
C(6)	4260 (3)	4840 (3)	7097 (3)
C(7)	3007 (3)	4444 (3)	5997 (3)
C(8)	2258 (3)	5688 (3)	5238 (3)
C(9)	2737 (2)	7381 (3)	5565 (3)
C(10)	3982 (2)	7767 (2)	6665 (3)
C(11)	4781 (2)	9410 (3)	7227 (3)
O(12)	4486 (2)	10816 (2)	6929 (2)
O(13)	7076 (2)	6634 (2)	9198 (2)
O(14)	8454 (2)	9220 (2)	6731 (2)
N(15)	9282 (2)	11400 (2)	8725 (2)
C(16)	8929 (4)	12725 (4)	10186 (4)
C(17)	10534 (3)	11533 (4)	7666 (4)
H–C(6)	4791 (34)	3963 (41)	7585 (37)
H–C(7)	2605 (33)	3262 (42)	5709 (39)
H–C(8)	1405 (36)	5392 (40)	4457 (40)
H–C(9)	2239 (34)	8239 (41)	5026 (37)
H_a–C(16)	9830 (38)	13328 (42)	10516 (39)
H_b–C(16)	8663 (35)	12222 (39)	11224 (42)
H_c–C(16)	8029 (38)	13303 (41)	10033 (38)
H_a–C(17)	10295 (35)	11507 (40)	6570 (46)
H_b–C(17)	11238 (36)	12254 (42)	8279 (40)
H_c–C(17)	11097 (36)	10427 (42)	7376 (38)

0.167 (2), 0.126 (6) and 0.196 (1) Å, respectively; (2) the plane of the substituents at N(1) (plane 3), *i.e.* in **3a** the phenyl group covering the atoms C(15) to C(20) and N(1) - the latter deviating only slightly from this plane by 0.043 (8) Å, causing an out-of-plane deformation of C(15)- and in **3b** a plane of N(15), C(16), C(17) and N(1).

The mentioned three planes are twisted from one another by rotations around the N(2),N(3)-, N(1),C(15)- or N(1),N(15)-bond, respectively (see *Table 4*). The large rotation around the N(2),N(3)-bond suggests for both molecules **3a** and **3b** that no conjugation exists between the phthalimido-π-system and the π-system of the NNO-grouping³), whereas the only slight rotation around the N(1),C(15)- and the N(1),N(15)-bond, respectively, indicates some conjugative interaction between the NNO-grouping and the substituent at N(1).

The non-conjugation between the phthalimido- and the NNO-groupings on one side and - at least in **3b** - a considerable conjugation between the NNO-grouping and the substituent at N(1) on the other side, express themselves also in the bond lengths (see *Table 5*). For a more general comparison of the bond lengths in **3a** and in **3b** with those in other diazenes with a semipolarly bonded

---

³) Compare the analogous findings in 1-phthalimidoazimines (**4**) [3].

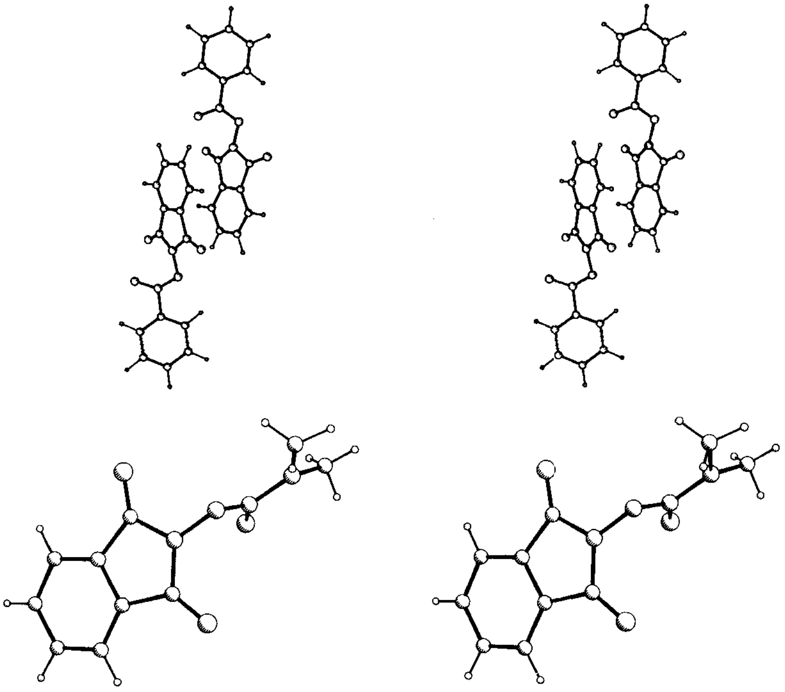
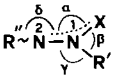


Fig. 1. *Stereopair views of* **3a**[2]) (upper part) *and* **3b** (lower part)

ligand X at one of the N-atoms (**6**), it seems useful to express the observed bond lengths in terms of total bond orders. Using the *Table 2* in [4], bond orders n for



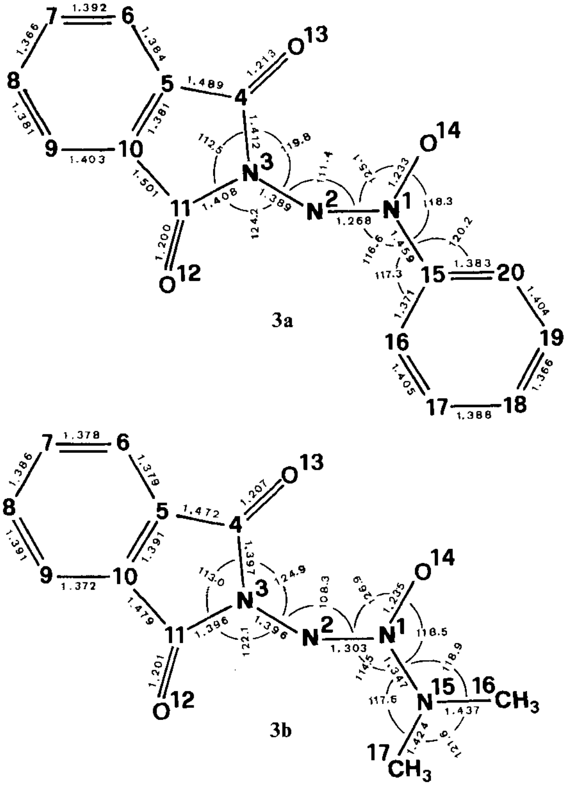
6

the bonds within the NNX-grouping of **6** and for the bonds to the nearest neighbour atoms in the substituents R' and R″ can be obtained as listed in *Table 5*.

The bond orders in the phenyl-substituted **3a** can be compared with those in the diazene-oxide **5a** - the only aryl substituted diazene-oxide for which, to our knowledge, so far a reliable structural analysis is at hand[4]) - and with those in in the azimines **4a** and **4b**, the latter two molecules being comparable with diazene-oxides since the *N*-phthalimido group resembles to some extend an O-atom bonded semipolarly to a N-skeleton [1] [2] [10]. In all examples of *Table 5* except **3b** (see below) the central N,N-bond exhibits a bond order of 1.8 and the N,X-bond of *ca.* 1.55 (when (*Z*)-configurated) and *ca.* 1.4 (when (*E*)-configurated), respectively. The difference in the bond orders of the N,N- and the N,O-bond

---

[4]) X-ray analyses of two other 1,2-diaryl-diazene-oxides (**5**, R = R' = p-$CH_3OC_6H_4$ [8] and p-$C_2H_5OC_6H_4$ [9], respectively) exhibit unreliable short N,N- and long N,C-bonds (cf. [4] [5]).



3a

3b

Fig. 2. *Numbering of atoms in* **3a** *and* **3b**. Bond lengths ($\sigma_{av} \approx 0.011$ Å for **3a** and 0.003 Å for **3b**) and some selected bond angles ($\sigma_{av} \approx 0.7°$ for **3a** and 0.2° for **3b**) are given

in **3a** points to the limitations of the comparableness of the *N*-phthalimido group with an O-atom. Complete comparableness should have led to equal bond orders as it is found for the two N,O-bonds of nitrobenzene with a bond order of 1.67 [11].

The bond lengths in **6** between N(1) and R′ and between N(2) and R″ correspond always to single bonds, again except for **3b**. For the N(2),N(3)-bond in **3a**, *i.e.* N(2),R″-bond in **6**, this is not unexpected regarding the conformational findings (see *Table 4*), whereas for the N(1),C(15)-bond in **3a**, *i.e.* N(1),R′ in **6**, a bond order > 1.0 could be expected due to conjugation as suggested by the conformational relation between the phenyl group and the NNO-function (see

Table 4. *Torsion angles*

Planes[a])	Torsion angles ($\sigma_{av} \approx 1°$)	
	3a	**3b**
1 to 2	60°	86°
2 to 3	5°	7°
1 to 3	55°	79°

[a]) Plane 1: NNO-function. Plane 2: phthalimido group. Plane 3: phenyl or dimethylamino.

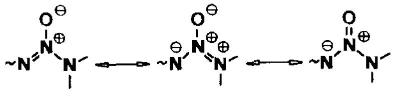
Table 5. *Bond lengths, bond orders n*[a]) *and bond angles in various diazenes with an semipolarly bonded substituent X on one N-atom* (see formula **6**)

Compound	Substitution pattern of **6**				Bond lengths and bond orders n[a])								Bond angles				Ref.
	X	R′	R″	Configuration	N(1),N(2)		N(1),X		N(1),R′		N(2),R″						
					Å	n	Å	n	Å	n	Å	n	α	β	γ	δ	
3a	O	C_6H_5	PN[b])	(*Z*)	1.268	1.82	1.233	1.57	1.459	1.00	1.389	1.08	125.1	118.3	116.6	111.4	this paper
4a	PN–N[b])	CH_3	CH_3	(*Z*)	1.268	1.82	1.301	1.56	1.486	< 1	1.455	1.02	122.3	122.9	114.8	112.7	[3]
4b	PN–N[b])	CH_3	CH_3	(*E*)	1.263	1.78	1.332	1.36	1.481	< 1	1.471	< 1	124.5	110.5	124.9	244.3	[3]
5a	O	C_6H_5	*p*-$CH_3C_6H_4$	(*E*)	1.265	1.80	1.264	1.45	1.470	< 1	1.427	1.02	125.0	114.3	120.5	240.8	[5]
3b	O	$N(CH_3)_2$	PN[b])	(*Z*)	1.303	1.55	1.235	1.56	1.347	1.40	1.396	1.06	126.9	118.5	114.5	108.3	this paper

[a]) Calculated from *Table 2* in [4]. The bond orders, naturally, have standard deviations equivalent to those of the bond lengths. [b]) PN = phthalimido.

Table 4) and the UV.-spectra of **3a** and its aryl-substituted derivatives [1]. The diazene-oxide **5a**, however, also exhibits bond orders of only 1.0 or even below for the two N, C-bonds (see *Table 5*).

The amino-substituted **3b** differs from the other examples in *Table 5* by, (1) equal bond orders for the N, N- and the N, O-bonds, and (2) relatively high bond orders for the N, R′- and the N, R″-bonds - the latter being still nearly a single bond as expected from the orthogonal orientation of the plane of the phthalimido group relative to the plane of the NNO-function (see *Table 4*). The equal bond orders for the N, N- and the N, O-bond indicate the similarity of the *N*-phthalimido group with an O-atom and its magnitude is the same as that of the two N, O-bonds in nitramines [12]. The bond order of 1.4 for the N(1), N(15)-bond in **3b** and the coplanarity of N(15) with its substituents C(16), C(17) and N(1) (see above) implies a substantial delocalization of the lone pair of electrons at N(15) into the NNO-function. This suggests to consider the amino-substituted molecules **3**. triazene-2-oxides (**7**), an almost unknown class of compounds. Only one cyclic member has been reported so far [13]. The chemical properties of this polyaza function seem to be worthy of further investigations.



7a **7b** **7c**

The bond angles around the N(1), N(2)-bond in **3a** and **3b** are quite comparable with the corresponding bond angles in **4a**, **4b** and **5a** (see *Table 5*). They

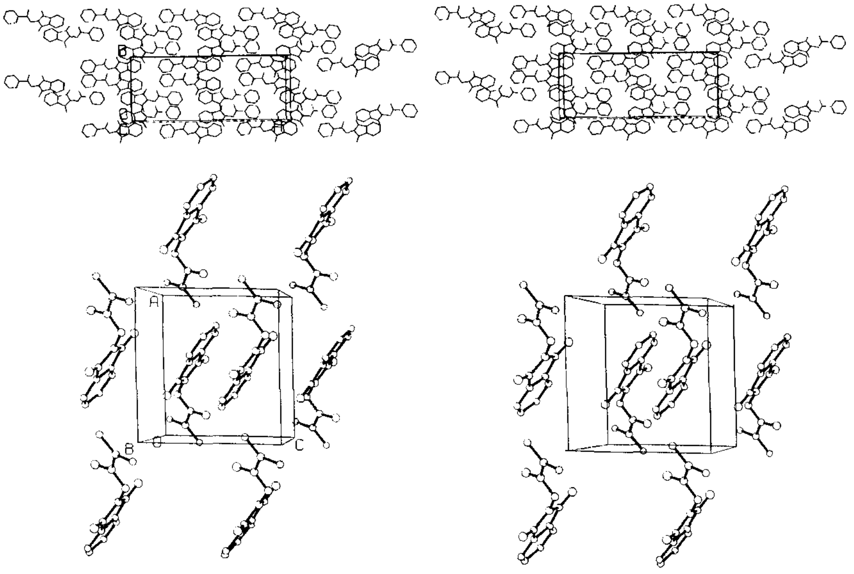


Fig. 3. *Packing diagrams of* **3a** (upper part) *and* **3b** (lower part)

are in agreement with the planar arrangement of the substituents at the two sp^2-hybridized N-atoms. The relatively large value of a is a consequence of steric (and perhaps electronic) repulsion between the O-atom and the phthalimido group which causes also the out-of-plane deformations of N(3), C(4) and C(11) in **3a** (see above). The low value of δ can be rationalized in terms of the VESPR-theory [14] as a consequence of the different electron-releasing power of ligands at N(2). The remarkably low value of δ in **3b** might also be a consequence of contributing resonance structures of type **7b** and **7c**.

The packing diagrams are shown in *Figure 3*. There are no unusually short intramolecular distances.

REFERENCES

[1] *L. Hoesch & B. Köppel*, Helv. Chim. Acta *64*, 864 (1981).

[2] *L. Hoesch*, Helv. Chim. Acta *64*, 890 (1981).

[3] *R. Moor, R. Grieb, A. Niggli, L. Hoesch & A.S. Dreiding*, Helv. Chim. Acta *62*, 1202 (1979).

[4] *R. Allmann*, 'Structural Chemistry', in *S. Patai* (ed.), 'The Chemistry of the Hydrazo, Azo and Azoxy Groups', Wiley-Interscience, London, New York, Sydney, Toronto 1975.

[5] *L. Hoesch & H.P. Weber*, Helv. Chim. Acta *60*, 3015 (1977).

[6] *P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq & M.M. Woolfson*, 'Multan 78. A System of Computer Program for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data'. York, England, and Louvain-la-Neuve, Belgium, 1978.

[7] *G.M. Sheldrick*, 'SHELX, Program for Crystal Structure Determination', University of Cambridge, England, 1976.

[8] *W.R. Krigbaum, Y. Chatani & P.G. Barber*, Acta Crystallogr. *B26*, 97 (1970).

[9] *W.R. Krigbaum & P.G. Barber*, Acta Crystallogr. *B27*, 1884 (1971).

[10] *L. Hoesch, M. Karpf, E. Dunkelblum & A.S. Dreiding*, Helv. Chim. Acta *60*, 816 (1977); *W. Schwotzer, C. Leuenberger, L. Hoesch, A.S. Dreiding & W. von Philipsborn*, Org. Magn. Reson. *9*, 382 (1977).

[11] *J. Trotter*, Acta Crystallogr. *12*, 884 (1959).

[12] *H.H. Cady, A.C. Larson & D.T. Cromer*, Acta Crystallogr. *16*, 617 (1963).

[13] *M.P. Serve, W.A. Feld, P.G. Seybold & R.N. Steppel*, J. Heterocycl. Chem. *12*, 811 (1975).

[14] *R.J. Gillespie*, «Molekülgeometrie», Verlag Chemie, Weinheim 1975.