C14	0.313 (1)	0.6266 (5)	0.1280 (2)	3.3 (2)
C15	0.124 (1)	0.6832 (5)	0.1482 (3)	4.7 (3)
C16	0.082 (1)	0.7903 (5)	0.1249 (4)	5.1 (4)
C17	0.227 (1)	0.8429 (5)	0.0818 (3)	5.1 (3)
C18	0.414 (1)	0.7905 (5)	0.0613 (3)	4.9 (3)
C19	0.457 (1)	0.6835 (5)	0.0848 (3)	4.1 (3)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

C1—C2	1.521 (7)	C8—C12	1.382 (8)
C1—C6	1.559 (9)	C9—C10	1.373 (8)
C1—C7	1.529 (8)	C10—C11	1.364 (8)
C2—C3	1.344 (7)	C11—C13	1.369 (9)
C2—C8	1.465 (7)	C12—C13	1.386 (8)
C3—C4	1.521 (7)	C14—C15	1.395 (9)
C3—C14	1.451 (7)	C14—C19	1.381 (8)
C4—C5	1.520 (9)	C15—C16	1.388 (9)
C4—C7	1.554 (9)	C16—C17	1.360 (9)
C5—C6	1.57 (1)	C17—C18	1.363 (9)
C8—C9	1.395 (7)	C18—C19	1.388 (8)
C2—C1—C6	105.8 (5)	C2—C8—C12	122.4 (5)
C2—C1—C7	100.8 (5)	C9—C8—C12	116.9 (5)
C6—C1—C7	99.9 (5)	C8—C9—C10	121.9 (6)
C1—C2—C3	107.6 (4)	C9—C10—C11	120.0 (6)
C1—C2—C8	123.2 (5)	C10—C11—C13	119.6 (5)
C3—C2—C8	129.0 (5)	C8—C12—C13	120.9 (6)
C2—C3—C4	106.5 (5)	C11—C13—C12	120.6 (6)
C2—C3—C14	128.9 (4)	C3—C14—C15	122.7 (6)
C4—C3—C14	122.5 (5)	C3—C14—C19	120.8 (5)
C3—C4—C5	106.1 (6)	C15—C14—C19	116.4 (5)
C3—C4—C7	101.4 (5)	C14—C15—C16	121.3 (7)
C5—C4—C7	101.6 (6)	C15—C16—C17	120.3 (7)
C4—C5—C6	102.0 (6)	C16—C17—C18	120.1 (6)
C1—C6—C5	103.1 (5)	C17—C18—C19	119.6 (7)
C1—C7—C4	93.0 (5)	C14—C19—C18	122.3 (6)
C2—C8—C9	120.6 (5)		

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry including angles involving H atoms, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71183 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1041]

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Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. I. 3-Cyano-4-(*n*-methoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadienes (n = 2, 3, 4)

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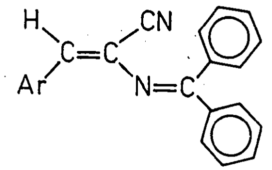
Abstract

The different position of the methoxy substituent in the three title 2-azabutadienes, 2MOPD, 3MOPD and 4MOPD [3-(2-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile, 3-(3-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile and 3-(4-methoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile], has a small influence on their geometry and conformation. The average bond lengths along the C=N—C=C fragment [1.286 (3), 1.405 (3) and 1.346 (3) Å] indicate a high degree of localization of the double and single bonds. The average torsion angle along the central N—C bond is 138°. The phenyl rings are tilted from the N=C($\mathrm{C_{Ph}}$)—$\mathrm{C_{Ph}}$ plane by 4.5 (1)-65.0 (1)°. The substituents around the C=C bond are arranged in a *Z* configuration. The molecules are packed by van der Waals forces.

Comment

The 2-azadienes are attractive starting compounds for the preparation of a variety of heterocyclic systems because of their ability to react as heterodienes in Diels–Alder reactions (Boger, 1983; Boger & Weinreb, 1987; Barluenda, Joglar, Gonzales & Fustero, 1990; Barluenda, Aznar, Fustero & Tomas, 1990). A convenient procedure for the synthesis of functionalized 2-azadienes has been reported (Dryanska, 1990) and applied (Dryanska, 1992) for the preparation of different 4-aryl-3-cyano-1,1-diphenyl-2-aza-1,3-butadienes (I).



(I)

The reaction is stereoselective and, in most cases, only one of the diastereoisomers is obtained. In similar compounds, such as dehydroamino acid derivatives (O'Donnell, Arasappan, Hornback & Huffman, 1990; Balsamini, Duranti, Mariani, Salvatori & Spadoni, 1990) and 4-arylidene-5(4*H*)-oxazolones (Rao & Filler, 1975) the major products were assigned the *Z* configuration based on the smaller (2.09-5.50 Hz) vicinal carbon-proton coupling constants compared with the larger (8.70-11.00 Hz) values for the minor diastereoisomers. The NMR data for substituted 2-azabutadienes (Dryanska, 1990), however, did not allow an unambiguous determination of their configuration. To elucidate the reaction stereochemistry and the molecular geometry of the diastereoisomers we have undertaken a series of structural investigations of the above compounds.

The interatomic distances and angles in the three structures are in excellent agreement and hereinafter the average molecular geometry will be discussed if not specifically mentioned. The sequence of bond lengths in the azabutadiene fragment indicates a certain localization of the C1=N1 and C2=C3 double bonds. The C1—N1 distance of 1.286 (3) Å corresponds well to the average value of 1.279 (8) Å for a $\mathrm{C_{ar}}$—C=N—C fragment calculated on the basis of 75 different compounds (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C2—C3 distance of 1.346 (3) Å is close to the value of 1.339 (11) Å for a conjugated $\mathrm{C_{ar}}$—C=C fragment calculated over 124 examples (Allen *et al.*, 1987). The central N1—C2 bond of 1.405 (3) Å is much longer than a similar conjugated single bond in imidazoles [1.376 (11) Å; Allen *et al.*, 1987]. This bond elongation and the large value of the C1—N1—C2—C3 torsion angle [within 135.4 (2)-139.5 (3)°] gives evidence of a diminished delocalization in the C=N—C=C linkage. The latter is probably caused by an intramolecular steric hindrance between the closely positioned cyano and *b* phenyl groups (Fig. 1). The packing of molecules 2MOPD, 3MOPD and 4MOPD is shown in Figs. 2, 3 and 4, respectively. Fig. 5 shows the three molecules superimposed on the C2—C4 bond.

The adjacent *a* and *b* phenyl rings are bonded to the azabutadiene at distances of 1.485 (3)-1.495 (3) Å, close to the typical distance [1.488 (12) Å; Allen *et al.*, 1987]. The *a* phenyl ring is rotated around the C1—C1*a* bond at 34.5 (2), 4.5 (8) and 9.9 (3)° for 2MOPD, 3MOPD and

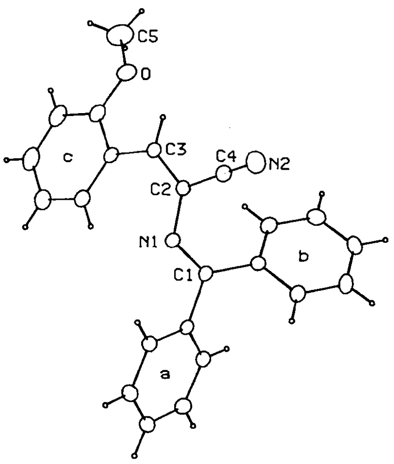


Fig. 1. *ORTEP* (Johnson, 1976) drawing of the 2MOPD molecule with the atom-numbering scheme and 10% probability thermal ellipsoids. H atoms are plotted as arbitrarily reduced spheres.

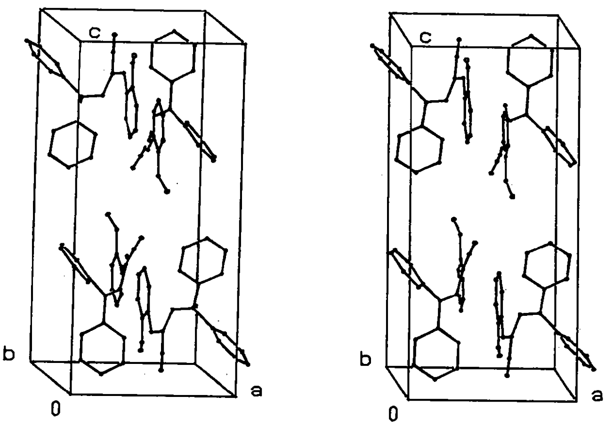


Fig. 2. Stereoscopic view of the molecular packing in 2MOPD.

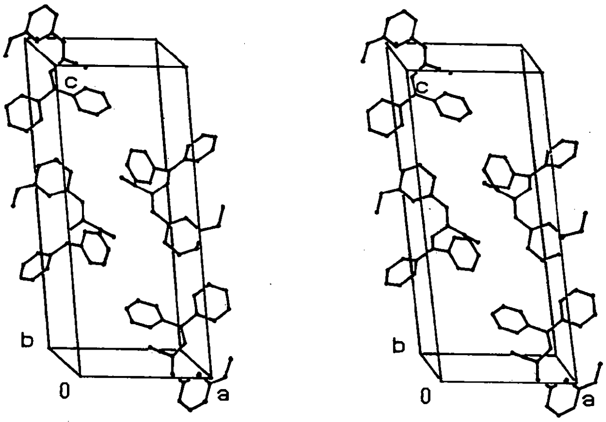


Fig. 3. Stereoscopic view of the molecular packing in 3MOPD.

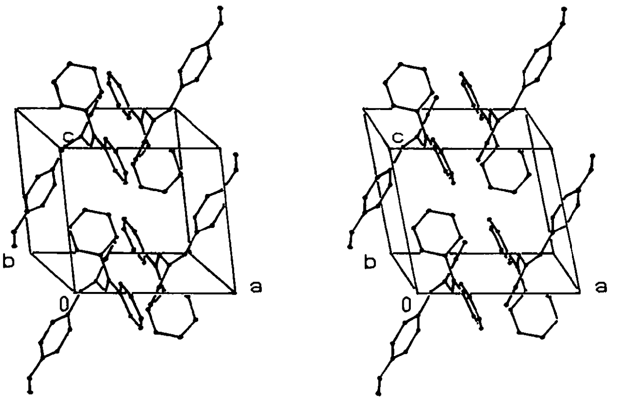


Fig. 4. Stereoscopic view of the molecular packing in 4MOPD.

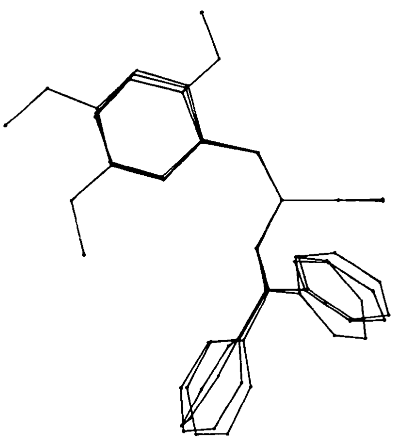


Fig. 5. View of the three molecules overlaid on the C2—C4 bond.

4MOPD, respectively. The second *b* phenyl ring is forced by the cyano group to rotate to larger angles, namely 46.71 (9), 58.95 (8) and 65.0 (1)°. It is noteworthy that the dihedral angle between the two phenyl rings lies in a relatively narrow range: 70.1 (1), 59.8 (1) and 71.9 (1)°, respectively. Analogously orientated phenyl rings were found in 8-(diphenylmethylene)amino-3,5,7-octatrien-2-one (Wong, 1978).

The methoxy-substituted *c* phenyl ring is bonded to the 2-azabutadiene fragment at a distance approximately 0.03 Å shorter than the *a* and *b* phenyl rings. The C1*c*—C3—C2 angle [128.3 (2), 129.9 (2) and 129.7 (2)° for 2MOPD, 3MOPD and 4MOPD, respectively] is remarkably large. The ring is tilted to the N(1)—C2(C4)═C3—C1*c* plane at different angles of 19.6 (1), 5.8 (5) and 5.2 (5)°. The methoxy group is almost coplanar with the phenyl ring, the greatest deviation of 0.256 (4) Å for C5 being that in 2MOPD and 0.079 (3) and 0.120 (3) Å for 3MOPD and 4MOPD, respectively. The intramolecular O···H3 separation in 2MOPD is 2.36 Å.

The three compounds are *Z* isomers like the major products in the synthesis of similar dehydroamino acid derivatives (O'Donnell *et al.*, 1990; Balsamini *et al.*, 1990) and 4-arylidene-5(4*H*)-oxazolones (Rao & Filler, 1975). Our tentative molecular-mechanics calculations (Crabbe & Appleyard, 1988) for 2MOPD indicated a relatively higher stability of the experimentally registered isomer: 53.680 kJ mol^{-1} for (*Z*)-2MOPD *versus* 54.330 kJ mol^{-1} for (*E*)-2MOPD.

Packing of the molecules is realized by van der Waals forces. Worth mentioning are a few contacts of the type C—H···*A*, where *A* = O, N. The closest hydrogen neighbours to the cyano N2 atom in 2MOPD are H53 $(x, 1+y, z)$ (N···H53 2.79 Å, N···H53—C5 124°) and H3*a* $(x, -y+\frac{1}{2}, z-\frac{1}{2})$ (N···H3*a* 2.76 Å, N···H3*a*—C3*a* 129°). Correspondingly, in 3MOPD, the shortest distances are O···H6*b* $(-x, 1-y, -z)$ 2.49 Å (O···H2*b*—C2*b* 160°) and N2···H3 $(-x-1, -y, -z)$ 2.54 Å (N2···H3—C3 170°). In 4MOPD, the methoxy O atom approaches H2*a* $(2-x, -y, -z)$ at 2.62 Å (O···H2*a*—C2*a* 158°) and the cyano N2 atom is at 2.59 Å to the H3*b* $(1-x, -1-y, 1-z)$ atom (N2···H3*b*—C3*b* 159°). No ring coupling or stacking takes place in either of the structures.

Experimental

2MOPD

Crystal data

$C_{23}H_{18}N_2O$
$M_r = 338.41$
Monoclinic
$P2_1/c$
$a = 9.371\ (2)$ Å
$b = 10.140\ (4)$ Å
$c = 19.471\ (2)$ Å
$\beta = 91.32\ (1)°$
$V = 1850\ (1)$ Å^3
$Z = 4$
$D_x = 1.215$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 19.97$–$20.55°$
$\mu = 0.07$ mm^{-1}
$T = 292$ K
Prismatic
0.4 × 0.3 × 0.2 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous-scan profiles
Absorption correction: none
7712 measured reflections
3620 independent reflections
2053 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 26°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 120 min
intensity variation: 0.3%

Refinement

Refinement on *F*
Final $R = 0.038$
$wR = 0.046$
$S = 1.297$
2053 reflections
235 parameters
H-atom parameters refined as riding

$w = 1/[\sigma^2(F) + (0.040F)^2]$
$(\Delta/\sigma)_{\rm max} = 0.021$
$\Delta\rho_{\rm max} = 0.171$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.167$ e Å^{-3}
Atomic scattering factors from *SDP*/*PDP* (Enraf-Nonius, 1985)

3MOPD

Crystal data

$C_{23}H_{18}N_2O$
$M_r = 338.41$
Monoclinic
$P2_1/c$
$a = 10.216\ (1)$ Å
$b = 7.706\ (1)$ Å
$c = 23.933\ (3)$ Å
$\beta = 100.13\ (1)^\circ$
$V = 1854.8\ (7)$ Å^3
$Z = 4$
$D_x = 1.211$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 18.18$–19.86°
$\mu = 0.06$ mm^{-1}
$T = 292$ K
Prismatic
0.34 × 0.32 × 0.28 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous-scan profiles
Absorption correction: none
4154 measured reflections
3927 independent reflections
1951 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 26^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 9$
$l = -29 \rightarrow 29$
1 standard reflection
frequency: 120 min
intensity variation: 0.1%

Refinement

Refinement on F
Final $R = 0.043$
$wR = 0.056$
$S = 1.606$
1951 reflections
235 parameters
H-atom parameters refined as riding

$w = 1/[\sigma^2(F) + (0.040F)^2]$
$(\Delta/\sigma)_{\rm max} = 0.161$
$\Delta\rho_{\rm max} = 0.154$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.125$ e Å^{-3}
Atomic scattering factors from *SDP/PDP* (Enraf-Nonius, 1985)

4MOPD

Crystal data

$C_{23}H_{18}N_2O$
$M_r = 338.41$
Triclinic
$P\overline{1}$
$a = 9.319\ (1)$ Å
$b = 10.391\ (1)$ Å
$c = 10.953\ (1)$ Å
$\alpha = 116.41\ (1)^\circ$
$\beta = 103.00\ (1)^\circ$
$\gamma = 91.49\ (1)^\circ$
$V = 915.8\ (4)$ Å^3
$Z = 2$

$D_x = 1.227$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 18.21$–18.90°
$\mu = 0.07$ mm^{-1}
$T = 292$ K
Prismatic
0.23 × 0.16 × 0.13 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous-scan profiles
Absorption correction: none
3827 measured reflections
3592 independent reflections
1969 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 26^\circ$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: 0.12%

Refinement

Refinement on F
Final $R = 0.042$
$wR = 0.051$
$S = 1.435$
1969 reflections
235 parameters
H-atom parameters refined as riding

$w = 1/[\sigma^2(F) + (0.040F)^2]$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.189$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.172$ e Å^{-3}
Atomic scattering factors from *SDP/PDP* (Enraf-Nonius, 1985)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* 2MOPD

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O	0.6489 (2)	−0.3904 (1)	0.56780 (8)	0.0609 (4)
N1	0.7231 (2)	0.0264 (2)	0.69925 (8)	0.0409 (4)
N2	0.6314 (3)	0.1559 (2)	0.5402 (1)	0.0817 (7)
C1	0.8302 (2)	0.1024 (2)	0.71142 (9)	0.0362 (5)
C2	0.6797 (2)	−0.0192 (2)	0.63392 (9)	0.0388 (5)
C3	0.6423 (2)	−0.1449 (2)	0.6202 (1)	0.0389 (5)
C4	0.6555 (2)	0.0778 (2)	0.5809 (1)	0.0503 (6)
C5	0.6729 (4)	−0.5137 (2)	0.5358 (2)	0.102 (1)
C1*a*	0.8468 (2)	0.1476 (2)	0.78378 (9)	0.0347 (5)
C2*a*	0.7260 (2)	0.1678 (2)	0.8223 (1)	0.0412 (5)
C3*a*	0.7377 (2)	0.2056 (2)	0.8903 (1)	0.0450 (6)
C4*a*	0.8709 (2)	0.2197 (2)	0.9210 (1)	0.0461 (6)
C5*a*	0.9920 (2)	0.1977 (2)	0.8834 (1)	0.0478 (6)
C6*a*	0.9804 (2)	0.1641 (2)	0.8147 (1)	0.0432 (5)
C1*b*	0.9370 (2)	0.1459 (2)	0.66040 (9)	0.0375 (5)
C2*b*	0.9798 (2)	0.2771 (2)	0.6574 (1)	0.0482 (6)
C3*b*	1.0780 (2)	0.3170 (2)	0.6102 (1)	0.0573 (6)
C4*b*	1.1384 (2)	0.2275 (2)	0.5666 (1)	0.0585 (7)
C5*b*	1.0996 (2)	0.0969 (2)	0.5699 (1)	0.0591 (7)
C6*b*	0.9983 (2)	0.0563 (2)	0.6163 (1)	0.0518 (6)
C1*c*	0.6469 (2)	−0.2586 (2)	0.6664 (1)	0.0386 (5)
C2*c*	0.6461 (2)	−0.3854 (2)	0.6378 (1)	0.0463 (6)
C3*c*	0.6445 (2)	−0.4964 (2)	0.6791 (1)	0.0632 (7)
C4*c*	0.6432 (3)	−0.4821 (2)	0.7500 (1)	0.0696 (7)
C5*c*	0.6448 (2)	−0.3589 (2)	0.7792 (1)	0.0627 (7)
C6*c*	0.6470 (2)	−0.2482 (2)	0.7381 (1)	0.0483 (6)

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* 3MOPD

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O	0.1804 (2)	0.3404 (3)	−0.02606 (8)	0.0775 (6)
N1	−0.1410 (2)	0.1671 (3)	0.09438 (8)	0.0493 (6)
N2	−0.4499 (2)	−0.0161 (4)	0.0949 (1)	0.102 (1)
C1	−0.1435 (2)	0.2476 (3)	0.14119 (9)	0.0432 (7)
C2	−0.2566 (2)	0.1283 (3)	0.0551 (1)	0.0547 (8)
C3	−0.2657 (2)	0.1414 (3)	−0.0014 (1)	0.0573 (8)
C4	−0.3660 (3)	0.0494 (4)	0.0769 (1)	0.0711 (9)
C5	0.2304 (3)	0.3239 (4)	0.0330 (1)	0.075 (1)
C1*a*	−0.0148 (2)	0.2616 (3)	0.18103 (9)	0.0409 (6)
C2*a*	0.0972 (2)	0.1771 (3)	0.1683 (1)	0.0488 (7)
C3*a*	0.2169 (2)	0.1844 (4)	0.2052 (1)	0.0564 (8)
C4*a*	0.2268 (2)	0.2735 (3)	0.2558 (1)	0.0565 (8)
C5*a*	0.1171 (2)	0.3582 (3)	0.2688 (1)	0.0528 (8)
C6*a*	−0.0025 (2)	0.3543 (3)	0.23128 (9)	0.0466 (7)
C1*b*	−0.2671 (2)	0.3251 (3)	0.15600 (9)	0.0448 (7)
C2*b*	−0.3159 (2)	0.2727 (4)	0.2038 (1)	0.0562 (8)
C3*b*	−0.4345 (2)	0.3395 (4)	0.2143 (1)	0.0699 (9)
C4*b*	−0.5042 (2)	0.4597 (4)	0.1782 (1)	0.0744 (9)
C5*b*	−0.4549 (2)	0.5146 (4)	0.1315 (1)	0.0707 (9)
C6*b*	−0.3366 (2)	0.4473 (3)	0.1201 (1)	0.0559 (8)
C1*c*	−0.1686 (2)	0.2034 (3)	−0.0346 (1)	0.0513 (7)
C2*c*	−0.2093 (3)	0.2162 (4)	−0.0933 (1)	0.0627 (8)
C3*c*	−0.1209 (3)	0.2735 (4)	−0.1267 (1)	0.072 (1)
C4*c*	0.0074 (3)	0.3147 (4)	−0.1034 (1)	0.0710 (9)
C5*c*	0.0498 (2)	0.2991 (4)	−0.0453 (1)	0.0570 (8)
C6*c*	−0.0377 (2)	0.2469 (3)	−0.0110 (1)	0.0533 (7)

Table 3. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* 4MOPD

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
O	1.3279 (2)	−0.0481 (2)	1.5922 (2)	0.0885 (6)
N1	0.7649 (2)	−0.1692 (2)	1.0384 (2)	0.0518 (5)
N2	0.5888 (2)	−0.5181 (2)	0.7915 (2)	0.0808 (8)
C1	0.7476 (2)	−0.1227 (2)	0.9456 (2)	0.0450 (6)
C2	0.7806 (2)	−0.3141 (2)	1.0050 (2)	0.0510 (7)
C3	0.8768 (2)	−0.3544 (2)	1.0891 (2)	0.0528 (7)
C4	0.6755 (3)	−0.4280 (2)	0.8829 (2)	0.0601 (7)
C5	1.3730 (3)	0.1036 (3)	1.6522 (3)	0.099 (1)
C1*a*	0.7236 (2)	0.0311 (2)	0.9932 (2)	0.0453 (6)
C2*a*	0.6951 (2)	0.1119 (2)	1.1237 (2)	0.0592 (7)
C3*a*	0.6766 (3)	0.2553 (2)	1.1679 (2)	0.0740 (9)
C4*a*	0.6857 (2)	0.3208 (2)	1.0844 (2)	0.0721 (9)
C5*a*	0.7136 (3)	0.2429 (2)	0.9560 (2)	0.0677 (8)
C6*a*	0.7324 (2)	0.0982 (2)	0.9095 (2)	0.0566 (7)
C1*b*	0.7601 (2)	−0.2094 (2)	0.7985 (2)	0.0468 (6)
C2*b*	0.6407 (3)	−0.2425 (2)	0.6828 (2)	0.0632 (8)
C3*b*	0.6542 (3)	−0.3255 (3)	0.5472 (2)	0.0801 (9)
C4*b*	0.7877 (3)	−0.3691 (3)	0.5266 (2)	0.085 (1)
C5*b*	0.9074 (3)	−0.3339 (3)	0.6390 (2)	0.0801 (9)
C6*b*	0.8940 (2)	−0.2555 (2)	0.7756 (2)	0.0601 (8)
C1*c*	0.9895 (2)	−0.2657 (2)	1.2201 (2)	0.0508 (6)
C2*c*	1.0711 (3)	−0.3365 (2)	1.2894 (2)	0.0662 (8)
C3*c*	1.1811 (3)	−0.2612 (2)	1.4125 (2)	0.0740 (8)
C4*c*	1.2151 (3)	−0.1119 (2)	1.4714 (2)	0.0621 (7)
C5*c*	1.1355 (2)	−0.0387 (2)	1.4065 (2)	0.0589 (7)
C6*c*	1.0248 (2)	−0.1152 (2)	1.2824 (2)	0.0559 (7)

Table 4. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

	2MOPD	3MOPD	4MOPD
O—C5	1.418 (3)	1.421 (3)	1.419 (3)
O—C2*c*	1.364 (3)		
O—C5*c*		1.370 (3)	
O—C4*c*			1.361 (2)
N1—C1	1.283 (2)	1.285 (3)	1.288 (3)
N1—C2	1.405 (2)	1.406 (3)	1.403 (3)
N2—C4	1.140 (3)	1.143 (4)	1.138 (2)
C1—C1*a*	1.487 (3)	1.485 (3)	1.486 (3)
C1—C1*b*	1.493 (3)	1.495 (3)	1.489 (3)
C2—C3	1.347 (3)	1.343 (4)	1.348 (3)
C2—C4	1.440 (3)	1.447 (4)	1.446 (2)
C3—C1*c*	1.462 (3)	1.457 (4)	1.452 (2)
C5—O—C2*c*	118.5 (2)		
C5—O—C5*c*		118.2 (2)	
C5—O—C4*c*			117.9 (2)
C1—N1—C2	125.0 (2)	122.9 (2)	122.4 (2)
N1—C1—C1*a*	115.2 (2)	116.4 (2)	116.9 (2)
N1—C1—C1*b*	126.0 (2)	123.1 (2)	124.5 (2)
C1*a*—C1—C1*b*	118.8 (2)	120.5 (2)	118.5 (2)
N1—C2—C3	124.0 (2)	123.9 (2)	123.8 (1)
N1—C2—C4	117.6 (2)	117.4 (2)	118.6 (2)
C3—C2—C4	117.9 (2)	118.2 (2)	117.1 (2)
C2—C3—C1*c*	128.3 (2)	129.9 (2)	129.7 (2)
N2—C4—C2	177.3 (2)	178.1 (3)	176.4 (3)
C2—N1—C1—C1*a*	174.4 (2)	173.4 (2)	176.6 (2)
C2—N1—C1—C1*b*	−6.6 (3)	−6.8 (4)	−7.6 (3)
C1—N1—C2—C3	135.4 (2)	139.5 (3)	139.5 (2)
C1—N1—C2—C4	−53.4 (3)	-48.4 (4)	−48.8 (3)
N1—C1—C1*a*—C2*a*	−32.9 (2)	−5.1 (3)	−11.0 (3)
N1—C1—C1*b*—C2*b*	135.1 (2)	120.2 (3)	118.8 (3)
N1—C2—C3—C1*c*	−4.3 (3)	−3.5 (5)	−5.5 (4)
C4—C2—C3—C1*c*	−175.5 (2)	−175.5 (3)	−177.3 (2)
C2—C3—C1*c*—C2*c*	−160.4 (2)	−174.8 (3)	177.6 (2)
C5—O—C2*c*—C3*c*	−9.8 (3)		
C5—O—C5*c*—C6*c*		1.9 (4)	
C5—O—C4*c*—C5*c*			−3.5 (3)

4MOPD was prepared as a single isomer according to a literature method (Dryanska, 1990). 2MOPD and 3MOPD were synthesized by the same procedure from *N*-diphenylmethyleneaminoacetonitrile (O'Donnell & Polt, 1982) and 2- and 3-methoxybenzaldehyde. While 3MOPD was obtained as a single isomer, the preparation of 2MOPD resulted in the formation of an *E*/*Z* mixture. After recrystallization of 2MOPD the major isomer was isolated. 2MOPD: m.p. 412-413 K (from ethanol); ^{1}H NMR (80 MHz, $CDCl_3$): δ 3.84 (*s*, 3H, CH_3O), 6.80-8.10 (*m*, 15H, alkene and aromatic H); elemental analysis, found (calc.): C 81.42 (81.63), H 5.48 (5.36), N 8.20 (8.28)%. 3MOPD: m.p. 372-374 K (from ethanol); ^{1}H NMR (80 MHz, $CDCl_3$): δ 3.68 (*s*, 3H, CH_3O), 6.61 (*s*, 1H, alkene H), 6.70-8.00 (*m*, 14H, aromatic H); elemental analysis, found (calc.): C 81.33 (81.63), H 5.58 (5.36), N 8.08 (8.28)%.

Data collection: CAD-4 software (Enraf-Nonius, 1988). Data reduction: *SDP*/*PDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*/*PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Maciček, 1992).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry including H-atom geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71223 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1035]

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Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. II. 3-Cyano-4-(*n*-fluorophenyl)-1,1-diphenyl-2-aza-1,3-butadienes (*n* = 2, 4)

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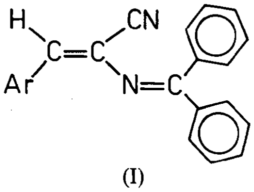
Abstract

The title compounds, 2FPD and 4FPD [3-(2-fluorophenyl)-2-(diphenylmethyleneamino)propenonitrile and 3-(4-fluorophenyl)-2-(diphenylmethyleneamino)propenonitrile], each crystallize in a *Z* configuration. The azabutadiene fragment in both 2FPD and 4FPD is twisted around the single N—C bond at 132.1 (3) and 129.2 (4)°, respectively. The non-substituted phenyl rings in 2FPD are tilted in respect to the $N1{=}C(C_{Ph}){—}C_{Ph}$ plane at 29.6 (1) and 51.3 (1)°; in 4FPD these angles are 21.7 (2) and 57.4 (2)°. The dihedral angle between these rings is 71.5 (1) (2FPD) and 71.7 (1)° (4FPD). The fluorophenyl ring in 2FPD is more rotated with respect to the planar $N{—}C(C_{CN}){=}CH{—}C_{Ph}$ group [15.2 (1)°] than that in 4FPD [5.2 (3)°]. No plane-to-plane coupling among the phenyl rings occurs. The molecular packing in both structures is dominated by van der Waals forces and the weak C—H···N bond to the cyano group [H3*c*···N 2.549 (3), 2.545 (3) Å, C3*c*—H3*c*···N 168.4 (3), 152.7 (3)°, in 2FPD and 4FPD, respectively].

Comment

2-Aza-1,3-dienes (I) are useful intermediates for the preparation of heterocyclic compounds (Boger & Weinreb, 1987; Barluenda, Joglar, Gonzales & Fustero, 1990; Barluenda, Aznar, Fustero & Tomas, 1990; Barluenda, Carlon, Pelaez, Joglar & Lopez Ortiz, 1992). Structural investigations on substituted 1,1-diphenyl-2-aza-1,3-butadienes were begun recently for three 3-cyano-4-(*n*-methoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadienes, MOPDs (*n* = 2, 3, 4) (Angelova, Macíček & Dryanska, 1993).



(I)

The title compounds are *Z* isomers like the MOPD analogues. Most interatomic distances and angles in both FPDs are equal within the e.s.d.'s to those in the three MOPDs. Notable differences were found only in 4FPD, where N1—C2 is longer by 0.019 Å than the average bond length of 1.405 (3) Å in 2FPD and the three MOPDs, while C3—C1*c* is shorter by 0.013 Å than the average bond length of 1.457 (5) Å.

Bond angles in the azabutadiene fragment substantially differ from the ideal for sp^2-hybridized C and N atoms, probably because of electron crowding and spatial hindrance between the cyano group and adjacent substituents. It is interesting that the largest angle C2—C3—C1*c* [128.7 (3) (2FPD) and 130.2 (3)° (4FPD)] is formed by the least obstructed substituent, *i.e.* the *c* phenyl ring. The C1—N1—C2—C3 torsion angles [132.1 (3) (2FPD) and 129.2 (4)° (4FPD)] are slightly smaller than the corresponding angles in the MOPDs [135.4 (2)-139.5 (3)° (Angelova *et al.*, 1993)].

A larger tilting of the *c* phenyl ring in 2FPD than in 4FPD is seen with the two molecules superimposed onto the central C2—C4 bond (Fig. 4). Similarly, in 2MOPD this angle [19.6 (1)°] is larger than in 3MOPD and 4MOPD [5.8 (5) and 5.2 (5)°, respectively (Angelova *et al.*, 1993)].

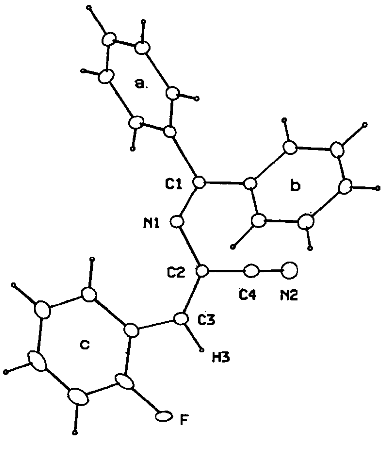


Fig. 1. *ORTEP* (Johnson, 1976) drawing of the 2FPD molecule with the atom-numbering scheme and 10% probabily thermal ellipsoids. H-atom spheres are arbitrarily reduced.

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