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2,2'-Azobis(1-morpholino-1-phenylethylene)

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Abstract. $C_{24}H_{28}N_4O_2$, $M_r = 404.5$, triclinic, $P\bar{1}$, $a = 6.040$ (1), $b = 13.466$ (4), $c = 14.626$ (4) Å, $\alpha = 111.03$ (3), $\beta = 99.92$ (2), $\gamma = 91.34$ (2)°, $V = 1089.1$ (5) Å³, $Z = 2$, $D_m = 1.22$, $D_x = 1.23$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.07$ mm⁻¹, $F(000) = 432$, room temperature, $R = 0.057$, $wR = 0.042$ for 3036 observed reflections [$I > 0.5\sigma(I)$]. The two molecules in the unit cell occupy sites of symmetry $\bar{1}$, and they have different conformations. The dihedral angle between the planes through the phenyl ring and the ethene system is 116.2 (2)° for molecule *A* and 125.6 (2)° for molecule *B*.

Introduction. The reaction of methyl azido(phenylhydrazono)acetate with enamines leads to different kinds of ring-closed products (Bruché, Garanti & Zecchi, 1985). However, the reaction with 1-morpholino-1-phenylethylene yields the title compound as the main product, whose structure has been determined by X-ray diffraction to confirm and complement the spectroscopic and analytical results. This study is connected with a line of research dealing with the synthetic potential of *C*-azidohydrazones.

Experimental. D_m by flotation in dilute K_2HgI_4 solution; yellow-orange prism $0.25 \times 0.20 \times 0.08$ mm. Intensity data collected with an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated $Mo\ K\alpha$ radiation, $\theta/2\theta$ scan technique, variable rate $2\text{--}10^\circ \text{ min}^{-1}$. Corrections for Lorentz and polarization but not for absorption. Structure solved using direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971), H atoms from difference Fourier synthesis.

Full-matrix least-squares refinement of scale factor, secondary-extinction parameter g (Larson, 1967, equation 3), anisotropic heavy atoms and isotropic H atoms; quantity minimized $\sum w(|F_o| - |F_c|)^2$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs used include *SDP* (Enraf–Nonius, 1979), *ORTEP* (Johnson, 1965) and various in-house programs for refinement and geometrical analysis running on a Gould 32/97 computer. Details of data collection and refinement listed in Table 1.

Table 1. *Details of data collection and structure refinement*

<i>(a)</i> Data collection	
Cell-parameter determination:	
No.; range of reflection (°)	25; 10–12
Range: <i>h</i>	0,7
<i>k</i>	–16,16
<i>l</i>	–17,17
θ (°)	0.0–25.0
Standard reflections	
No.; variation of intensity	3; 2%
No. of intensity measurements	3818
No. of unique reflections	3818
<i>(b)</i> Refinement	
Refined reflections:	
No.; criterion for use	3036; $I > 0.5\sigma(I)$
<i>R</i> ; <i>wR</i>	0.057; 0.042
Goodness of fit, <i>S</i>	1.25
Weighting scheme; <i>a</i>	$w = 4F_o/[\sigma^2(F_o^2) + aF_o^2]$; 0.0004
$(\Delta/\sigma)_{\max}$ in the last cycle	< 0.01
$ \Delta\rho _{\max}$ in final difference Fourier map ($e\ \text{Å}^{-3}$)	0.2
Extinction coefficient $g(\times 10^6)$	18 (2)

Discussion. Atom coordinates and equivalent isotropic temperature factors are given in Table 2.* The molecule *B* with the numbering scheme is given in Fig. 1; molecule *A* (not shown) has the same atom labeling. On the whole, the highest differences between corresponding bond distances, angles and absolute values of torsion angles of the two molecules are 0.024 Å, 2.1° and 10°, respectively. From Table 3 we note differences greater than 1° between corresponding bond angles in the phenyl and morpholino rings. The morpholino group of molecule *B* has 'approximate' *m* symmetry through O and N(2) with puckering coordinates (Cremer & Pople, 1975) $Q=0.549(3)$ Å, $\varphi=178(4)$ and $\theta=4.8(3)^\circ$. On the other hand, the morpholino ring of molecule *A* shows a significant distortion from *m* symmetry with a pseudo-twofold axis through the midpoints of the C(10)–O and N(2)–C(12) bonds and puckering parameters $Q=0.560(3)$ Å, $\varphi=154(6)$ and $\theta=2.9(3)^\circ$.

The packing of the molecules in the crystal does not reveal particularly short contacts.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43213 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final coordinates and equivalent isotropic thermal parameters, *e.s.d.*'s in parentheses

$$U_{eq} = (\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j) / 6\pi^2.$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{Å}^2)$
Molecule A				
O	0.3107 (3)	0.0693 (1)	0.0619 (1)	0.0635 (8)
N(1)	0.5522 (3)	0.0354 (1)	0.4895 (1)	0.0476 (8)
N(2)	0.4698 (3)	0.1041 (1)	0.2663 (1)	0.0432 (7)
C(1)	0.5638 (3)	0.0967 (2)	0.3571 (1)	0.0408 (9)
C(2)	0.4803 (4)	0.0274 (2)	0.3921 (2)	0.048 (1)
C(3)	0.7527 (4)	0.1795 (2)	0.4185 (1)	0.0403 (9)
C(4)	0.9643 (4)	0.1536 (2)	0.4491 (2)	0.051 (1)
C(5)	1.1397 (4)	0.2316 (2)	0.5039 (2)	0.062 (1)
C(6)	1.0980 (5)	0.3369 (2)	0.5306 (2)	0.064 (1)
C(7)	0.8906 (5)	0.3650 (2)	0.5028 (2)	0.065 (1)
C(8)	0.7154 (4)	0.2867 (2)	0.4459 (2)	0.053 (1)
C(9)	0.2672 (4)	0.0338 (2)	0.2084 (2)	0.056 (1)
C(10)	0.1619 (5)	0.0693 (3)	0.1266 (2)	0.064 (1)
C(11)	0.5052 (4)	0.1412 (2)	0.1180 (2)	0.054 (1)
C(12)	0.6230 (4)	0.1103 (2)	0.2011 (2)	0.047 (1)
Molecule B				
O	−0.1770 (3)	0.8649 (1)	0.2064 (1)	0.080 (1)
N(1)	0.4442 (3)	0.4976 (1)	0.0330 (1)	0.0484 (8)
N(2)	0.0311 (3)	0.6706 (1)	0.1503 (1)	0.0459 (7)
C(1)	0.1852 (3)	0.5937 (2)	0.1311 (2)	0.0429 (9)
C(2)	0.3101 (4)	0.5817 (2)	0.0604 (2)	0.047 (1)
C(3)	0.1894 (4)	0.5226 (2)	0.1889 (1)	0.0410 (9)
C(4)	0.3879 (4)	0.5041 (2)	0.2400 (2)	0.053 (1)
C(5)	0.3861 (5)	0.4361 (2)	0.2911 (2)	0.065 (1)
C(6)	0.1866 (5)	0.3840 (2)	0.2908 (2)	0.063 (1)
C(7)	−0.0117 (5)	0.4028 (2)	0.2402 (2)	0.060 (1)
C(8)	−0.0110 (4)	0.4716 (2)	0.1904 (2)	0.049 (1)
C(9)	−0.0109 (5)	0.7305 (2)	0.0850 (2)	0.057 (1)
C(10)	−0.2079 (5)	0.7947 (2)	0.1047 (2)	0.068 (1)
C(11)	−0.1521 (7)	0.8043 (3)	0.2684 (3)	0.076 (2)
C(12)	0.0473 (5)	0.7402 (2)	0.2556 (2)	0.061 (1)

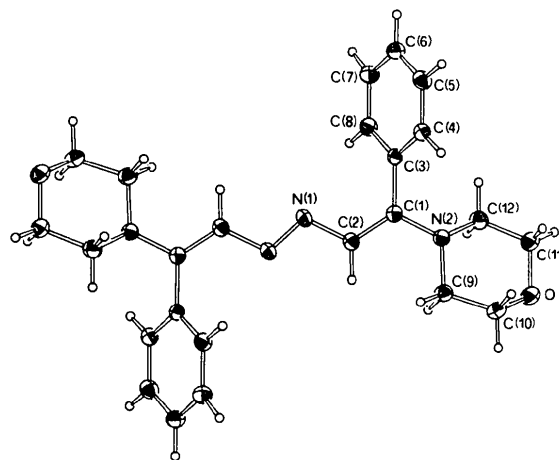


Fig. 1. View of molecule *B* with numbering scheme. Thermal ellipsoids for heavy atoms are at 20% probability level; H atoms are not to scale.

Table 3. Bond distances (Å) and bond angles (°), *e.s.d.*'s in parentheses

	Molecule A	Molecule B
O–C(10)	1.413 (4)	1.424 (3)
O–C(11)	1.426 (3)	1.414 (5)
N(1)–N(1')	1.285 (5)	1.287 (5)
N(1)–C(2)	1.381 (3)	1.388 (3)
N(2)–C(1)	1.391 (3)	1.394 (3)
N(2)–C(9)	1.457 (3)	1.452 (4)
N(2)–C(12)	1.460 (3)	1.472 (3)
C(1)–C(2)	1.341 (4)	1.349 (4)
C(1)–C(3)	1.490 (3)	1.486 (4)
C(3)–C(4)	1.375 (3)	1.378 (3)
C(3)–C(8)	1.388 (3)	1.385 (4)
C(4)–C(5)	1.386 (3)	1.375 (5)
C(5)–C(6)	1.372 (4)	1.379 (5)
C(6)–C(7)	1.355 (4)	1.375 (4)
C(7)–C(8)	1.393 (4)	1.369 (4)
C(9)–C(10)	1.492 (5)	1.495 (4)
C(11)–C(12)	1.495 (4)	1.497 (5)
C(10)–O–C(11)	108.9 (2)	109.3 (3)
C(2)–N(1)–N(1')	112.5 (1)	112.2 (2)
C(9)–N(2)–C(12)	110.5 (2)	111.3 (2)
C(1)–N(2)–C(12)	117.6 (2)	116.2 (2)
C(1)–N(2)–C(9)	117.4 (2)	118.3 (2)
N(2)–C(1)–C(3)	114.8 (2)	115.2 (2)
N(2)–C(1)–C(2)	123.4 (2)	121.6 (2)
C(2)–C(1)–C(3)	121.6 (2)	123.1 (2)
N(1)–C(2)–C(1)	121.3 (2)	121.7 (2)
C(1)–C(3)–C(8)	119.2 (2)	119.4 (2)
C(1)–C(3)–C(4)	122.3 (2)	121.9 (2)
C(4)–C(3)–C(8)	118.4 (2)	118.6 (2)
C(3)–C(4)–C(5)	121.6 (3)	120.4 (3)
C(4)–C(5)–C(6)	118.8 (3)	120.7 (3)
C(5)–C(6)–C(7)	121.0 (3)	118.9 (3)
C(6)–C(7)–C(8)	120.2 (3)	120.6 (3)
C(3)–C(8)–C(7)	119.9 (3)	120.7 (3)
N(2)–C(9)–C(10)	109.7 (3)	111.1 (2)
O–C(10)–C(9)	112.1 (2)	111.6 (3)
O–C(11)–C(12)	111.4 (2)	111.7 (3)
N(2)–C(12)–C(11)	111.0 (2)	110.8 (2)

(i) Symmetry transformation: (1–*x*, –*y*, 1–*z*) for molecule *A* and (1–*x*, 1–*y*, –*z*) for molecule *B*.

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Structures of Substituted Perfluoropolyphenyls. IV. Structure of 2-Bromononafluorobiphenyl

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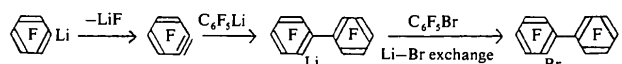
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Abstract. $C_{12}BrF_9$, $M_r = 395.041$, orthorhombic, $Pbca$, $a = 12.610$ (5), $b = 23.565$ (5), $c = 8.029$ (4) Å, $U = 2385.85$ Å³, $Z = 8$, $D_m = 2.183$, $D_x = 2.200$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 34.40$ cm⁻¹, $F(000) = 1504$, $T = 293$ K. Final $R = 0.055$ for 988 observed reflections with $I > 3\sigma(I)$. The dihedral angle between the rings is 79.6 (10)° and the inter-ring bond length is 1.502 (15) Å (uncorrected for thermal libration).

Introduction. 2,2'-Disubstitution of perfluorobiphenyl with bromine has no significant effect on the inter-ring bond length of 1.486 (5) Å, but increases the dihedral angle from 59.5 to 75.9 (5)° (Gleason & Britton, 1976; Hamor & Hamor, 1980). This analysis investigates the effect on these two parameters of 2-substitution with bromine, and is the fourth in a series of investigations into the correlation between inter-ring bond length and dihedral angle in substituted perfluoropolyphenyls.

On the assumption of an aryne mechanism it was proposed that 2-bromononafluorobiphenyl would be formed from pentafluorophenyllithium (Fenton, Park, Shaw & Massey, 1964; Fenton & Massey, 1965), according to the following scheme:



Our confirmation of the structure of the product affords further evidence for this mechanism.

Experimental. Preparation by the method of Fenton, Park, Shaw & Massey (1964); D_m measured pycnometrically; colourless, rectangular block-shaped crystals obtained from ethanol; crystal, $0.38 \times 0.27 \times 0.12$ mm, sealed in a Lindemann-glass capillary, mounted about c ; preliminary lattice constants determined from oscillation and Weissenberg photographs;

refined lattice constants from a Stoe Stadi-2 two-circle diffractometer, using axial-row reflections (θ range $11 \rightarrow 32^\circ$); no correction for absorption and extinction; $2\theta_{\text{max}} = 60^\circ$; index range: $0 \leq h \leq 14$; $0 \leq k \leq 30$; $0 \leq l \leq 8$; one standard reflection every 50 reflections, no significant change; 3072 reflections measured, 2699 being unique and 988 having $I > 3\sigma(I)$; Br located by Patterson synthesis, other atoms by successive ΔF syntheses; anisotropic refinement by full-matrix least squares on F with unit weights gave final $R = 0.055$; $\Delta/\sigma \geq 0.001$; $\Delta\rho$ excursions = $+0.67$ to -0.75 e Å⁻³, maximum and minimum density occurring near the Br positions; scattering factors from Cromer & Mann (1968); calculations carried out with *SHELX76* (Sheldrick, 1976) implemented at Loughborough University of Technology Computer Centre, and with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) implemented at the University of Manchester Regional Computer Centre.*

Discussion. Final positional parameters are listed in Table 1, and bond lengths and angles in Table 2. The molecular structure, with atom numbering, is given in Fig. 1, and the c -projection of the cell contents is shown in Fig. 2.

The confirmation that the structure of the reaction product is indeed 2-bromononafluorobiphenyl strengthens the evidence for the proposed aryne mechanism (Fenton, Park, Shaw & Massey, 1964; Fenton & Massey, 1965).

* Lists of structure factors, anisotropic thermal parameters, intermolecular contacts, geometric and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43227 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.