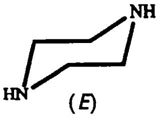
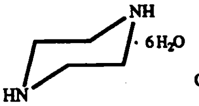
prefer the equatorial orientation. Fig. 1 shows that the piperazine ring in *trans*-2,2,5,5-tetracyano-3,6-diphenylpiperazine–propanone (1/2) (*D*) is in the chair conformation and that the phenyl rings occupy equatorial positions. There are two propanone solvent molecules per piperazine unit and there is no hydrogen bonding between the propanone molecules. The closest distances (2·43 Å) between molecules in the unit cell are between the hydrogen on N(1) of piperazine and the oxygen O(1) of propanone. All exterior and interior bond angles of the piperazine ring system in (*D*) are approximately tetrahedral.

The C(1)—N(1)—C(2) bond angle of 113·9 (2)° in the highly substituted piperazine (*D*) is larger than the C—N—C bond angles observed in gaseous piperazine (*E*), 109·0 (8)° (Yokozeki & Kuchitsu, 1971), in piperazine hexahydrate (*F*), 109·3 (3)° (Schwarzenbach, 1968), in piperazine dihydrogen dichloride monohydrate (*G*), 110·9° (Rérat, 1960), in *trans*-2,5-dimethylpiperazine (*H*), 110·9 (2)° (Okamoto, Sekido, Ono, Noguchi & Hirokawa, 1982), and in *trans*-2,5-dimethylpiperazine dihydrogen dichloride (*I*), 112·4 (3)° (Bart, Bassi & Scordamaglia, 1978).

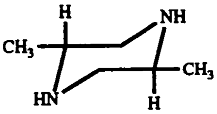


(*E*)

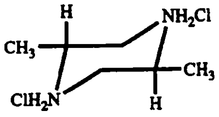


(*F*)

(*G*)



(*H*)



(*I*)

The C(1)—N(1) and C(2)—N(1) interatomic distances of 1·454 (3) and 1·455 (3) Å, respectively, in piperazine (*D*) are in the lower range of the C—N bond lengths (1·46 to 1·51 Å) of those found in other piperazine studies [(*E*) 1·467 (4), (*F*) 1·458 (4) and 1·459 (4), (*G*) 1·490 and 1·509, (*H*) 1·463 (3) and 1·465 (3), and (*I*) 1·509 (9) Å]. The C(1)—C(2′) bond lengths [1·569 (4) Å] in the piperazine ring of (*D*) are longer than the corresponding C—C bond lengths in the piperazines (*E*) [1·540 (8)], (*F*) [1·491 (5)], (*G*) (1·527), (*H*) [1·521 (3)] and (*I*) [1·534 (12) Å].

Funds for the purchase of the Nicolet *R*3*m*/*V* diffractometer system were made available from the National Science Foundation under grant CHE-85-14495, and we thank the Niels Clauson–Kaas Laboratory, Farnum, Denmark, for the generous sample of aminomalononitrile tosylate (AMNT).

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Structure of (*E*,*E*)-4-Amino-3-cyano-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene

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Abstract. (*E*,*E*)-4-Amino-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene-3-carbonitrile, $C_{11}H_{11}N_3O_2$, $M_r = 217{\cdot}20$, monoclinic, $P2_1/n$, $a = 8{\cdot}6958\ (11)$, $b = 10{\cdot}4009\ (12)$, $c = 12{\cdot}297\ (3)$ Å, $\beta = 107{\cdot}174\ (15)°$, $V = 1062{\cdot}6\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·710730 Å, μ = 0·090 mm^{-1}, $F(000)$ =

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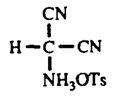
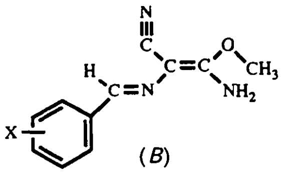
456, $T = 183$ K, final $R = 0{\cdot}048$ for 2295 observed reflections. The structure consists of a conformation which contains two *trans* (*E*) double bonds. The 4-hydroxyphenyl ring is essentially coplanar with the imine (C=N) double bond and there is a *cis* (*Z*) relationship between the cyano and methoxy groups.

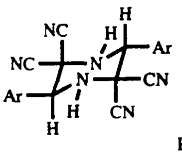
Introduction. Aminopropanedinitrile 4-methylbenzenesulfonate [aminomalononitrile *p*-toluenesulfonate (*A*)] reacts with aromatic aldehydes in methanolic sodium ethanoate to afford (*E*,*E*)-4-amino-1-aryl-3-cyano-4-methoxy-2-aza-1,3-butadienes (*B*) and *trans*-2,2,5,5-tetracyano-3,6-diarylpiperazines (*C*) (Kim, 1989; Freeman & Kim, 1989, 1991). Highly functionalized 2-aza-1,3-butadienes are important in Diels–Alder reactions of heterodienes and in mechanistic studies of cycloaddition reactions (Boger & Weinreb, 1987). Infrared, ^{13}C NMR, ^{1}H NMR and ultraviolet–visible spectra, and elemental analyses confirm the empirical formula of these 2-aza-1,3-butadienes (*B*) but cannot distinguish among the four possible diastereomers.



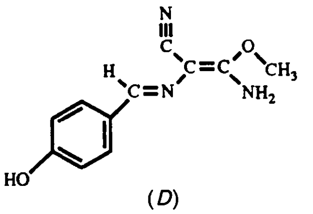
(*A*)



(*B*)



(*C*)



(*D*)

Table 1. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^4$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	.	U_{eq}
C(1)	15725 (15)	12330 (12)	11651 (10)	227 (4)
C(2)	30452 (15)	− 4396 (12)	7030 (10)	237 (4)
C(3)	36004 (15)	− 12189 (12)	948 (10)	232 (4)
C(4)	30284 (17)	− 10311 (12)	− 12744 (11)	253 (4)
C(5)	35678 (17)	− 17929 (13)	− 20066 (11)	276 (4)
C(6)	46969 (16)	− 27497 (12)	− 15788 (11)	254 (4)
C(7)	52869 (16)	− 29529 (13)	− 4106 (11)	270 (4)
C(8)	47295 (16)	− 21905 (13)	3201 (11)	264 (4)
C(9)	5501 (15)	22634 (12)	7701 (10)	217 (4)
C(10)	20441 (15)	9474 (12)	23387 (10)	230 (4)
C(11)	− 10183 (17)	39839 (13)	11761 (12)	282 (4)
N(1)	20758 (13)	5059 (10)	3776 (8)	229 (3)
N(2)	540 (15)	25821 (12)	− 3272 (9)	279 (4)
N(3)	24420 (14)	6217 (11)	32759 (9)	304 (4)
O(1)	1122 (12)	29459 (9)	15446 (7)	277 (3)
O(2)	51691 (14)	− 34770 (10)	− 23508 (8)	359 (4)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(9)	1·386 (2)	C(1)—C(10)	1·411 (2)
C(1)—N(1)	1·397 (2)	C(2)—C(3)	1·460 (2)
C(2)—N(1)	1·280 (2)	C(3)—C(4)	1·401 (2)
C(3)—C(8)	1·396 (2)	C(4)—C(5)	1·381 (2)
C(5)—C(6)	1·388 (2)	C(6)—C(7)	1·391 (2)
C(6)—O(2)	1·368 (2)	C(7)—C(8)	1·389 (2)
C(9)—N(2)	1·332 (2)	C(9)—O(1)	1·330 (2)
C(10)—N(3)	1·152 (2)	C(11)—O(1)	1·440 (2)
C(9)—C(1)—C(10)	119·0 (1)	C(9)—C(1)—N(1)	118·4 (1)
C(10)—C(1)—N(1)	122·6 (1)	C(3)—C(2)—N(1)	122·3 (1)
C(2)—C(3)—C(4)	122·1 (1)	C(2)—C(3)—C(8)	119·5 (1)
C(4)—C(3)—C(8)	118·4 (1)	C(3)—C(4)—C(5)	120·6 (1)
C(4)—C(5)—C(6	120·2 (1)	C(5)—C(6)—C(7)	120·3 (1)
C(5)—C(6)—O(2)	117·2 (1)	C(7)—C(6)—O(2)	122·5 (1)
C(6)—C(7)—C(8)	119·2 (1)	C(3)—C(8)—C(7)	121·3 (1)
C(1)—C(9)—N(2)	122·0 (1)	C(1)—C(9)—O(1)	116·8 (1)
N(2)—C(9)—O(1)	121·1 (1)	C(1)—C(10)—N(3)	175·0 (1)
C(1)—N(1)—C(2)	120·8 (1)	C(9)—O(1)—C(11)	119·2 (1)

Experimental. Crystals of (*E*,*E*)-4-amino-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene-3-carbonitrile (*D*) were grown by slow evaporation from a solution of the compound in propanone–petroleum ether (303–333 K). A dark-orange crystal of approximate dimensions 0·23 × 0·34 × 0·60 mm was oil mounted on a glass fiber. Data were collected on a Nicolet *P*3 diffractometer equipped with a modified LT-2 apparatus using standard techniques (Churchill, Lashewycz & Rotella, 1977). θ–2θ scans for $2\theta = 4{\cdot}0$ to $55{\cdot}0°$ ($0 \leq h \leq 11$, $0 \leq k \leq 13$, $-15 \leq l \leq 15$) yielded 2620 reflections which were merged to 2295 unique reflections ($R_{\text{int}} = 1{\cdot}13\%$) with $|F_o| > 0$. Standard reflections 600, 060, 105 showed no variation or decay during data collection. Data were corrected for Lorentz and polarization effects and for extinction $\{\chi = 0{\cdot}0032\,(8)$ where $F^* = F[1 + 0{\cdot}002\chi F^2/\sin(2\theta)]^{-1/4}\}$. The space group was determined to be $P2_1/n$ from systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. Crystallographic calculations were carried out using either our locally modified version of the *UCLA* package (Strouse, 1981) or the *SHELXTL-Plus* program set (Sheldrick, 1988). The analytical scattering factors for neutral atoms were used throughout the analysis; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included (*International Tables for X-ray Crystallography*, 1974, Vol. IV, pp. 99–101, 149–150). The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0{\cdot}0010(|F_o|)^2$. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F using *SHELXTL-Plus*. All 16 non-H atoms were located from the initial electron density map. H-atom positions were determined from a series of difference Fourier calculations. Refinement of positional and thermal parameters (isotropic for H atoms) converged to $R = 0{\cdot}048$, $wR = 0{\cdot}058$ and GOF = 1·33 for 190 variables refined against all 2295 non-zero data [$R = 0{\cdot}035$, $wR = 0{\cdot}052$ for those 1840 data with $|F_o| > 6{\cdot}0\sigma(|F_o|)$]. A final difference Fourier map was devoid of significant features, $\rho_{\max} = 0{\cdot}24$, $\rho_{\min} = -0{\cdot}28\ \text{e Å}^{-3}$. The largest and mean Δ/σ in the final refinement cycle were 0·001 and < 0·001, respectively.*

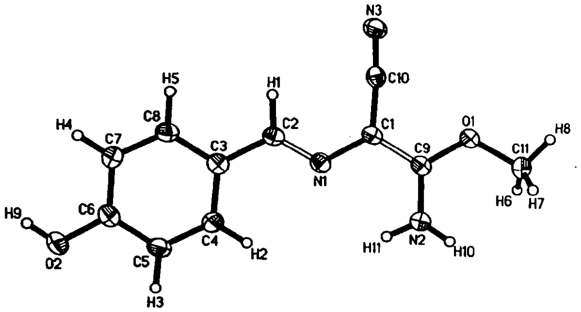


Fig. 1. *ORTEP* view (Johnson, 1976) of the molecular structure and atom numbering of (*E,E*)-4-amino-3-cyano-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene (*D*). Thermal ellipsoids are drawn at the 50% probability level.

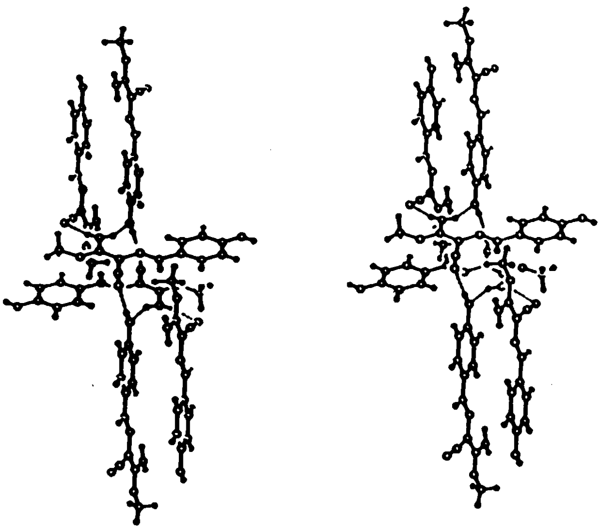
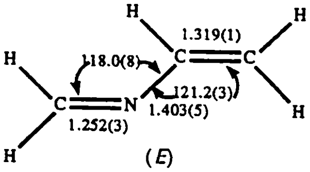


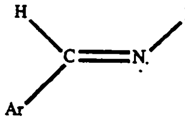
Fig. 2. Stereodiagram illustrating close intermolecular contacts for (*E,E*)-4-amino-3-cyano-1-(4-hydroxyphenyl)-4-methoxy-2-aza-1,3-butadiene (*D*) [H(9)—N(3) = 2·08, H(11)—O(2) = 2·27, H(10)—N(3) = 2·18 Å].

Discussion. The atomic coordinates for the highly functionalized 2-aza-1,3-butadiene (*D*) are shown in Table 1 and bond lengths and angles in Table 2. The molecular structure is shown in Fig. 1 and a stereodiagram showing intermolecular hydrogen bonding between the amino group and the N atom of the cyano group and between the amino group and the O atom of the hydroxyl group is presented in Fig. 2.

The geometry of the highly substituted 2-aza-1,3-butadiene (*D*) is that of the *trans,trans* (*E,E*) diastereomer. This is consistent with *ab initio* molecular-orbital calculations (Bock, George & Trachtman, 1984) and the microwave spectrum (Sugie, Takeo & Matsumura, 1989) of 2-aza-1,3-butadiene (*E*) which show that the *trans* conformer of (*E*) is more stable than the *cis* conformer. It is of interest to compare the structure of 2-aza-1,3-butadiene (*E*) with the more highly substituted 2-aza-1,3-butadiene (*D*).



(*E*)



(*F*)

The longer C(2)—N(1) and C(1)—C(9) bond lengths of 1·280 (2) and 1·386 (2) Å, respectively, in 2-aza-1,3-butadiene (*D*) suggest less double-bond character than in the corresponding bonds in 2-aza-1,3-butadiene (*E*). These results, the larger C(2)—N(1)—C(1) and N(1)—C(1)—C(9) bond angles [120·8 (1) and 118·4 (1)°, respectively] in (*D*) and the extended conjugation involving the 4-hydroxyphenyl substituent are consistent with greater π-electron delocalization (resonance) in the more highly substituted 2-aza-1,3-butadiene (*D*) than in 2-aza-1,3-butadiene (*E*). In addition, considerable evidence indicates that the preferred conformation of imines is the stable *trans* (*F*) form in which the aryl ring is essentially coplanar with the imine double bond (Odian, Yang & Wei, 1985; Al-Rawi & Saleem, 1989).

Funds for the purchase of the Nicolet *R3m/V* diffractometer system were made available from the National Science Foundation under grant CHE-85-14495, and we thank the Niels Clauson-Kaas Laboratory, Farnum, Denmark, for the generous sample of aminomalononitrile tosylate (AMNT).

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* Lists of structure factors, anisotropic displacement coefficients, H-atom coordinates, hydrogen-bond lengths and angles, and a perspective diagram of the structure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54105 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 4-Cyano-4′-iodobiphenyl at 297 and 183 K

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Abstract. 4′-Iodobiphenyl-4-carbonitrile, $C_{13}H_8IN$, M_r = 305·12, monoclinic, $P2_1/c$, Z = 8, Mo $K\alpha$, λ = 0·71069 Å, F(000) = 1168. At 297 (2) K, a = 9·854 (2), b = 14·869 (3), c = 17·103 (5) Å, β = 115·44 (2)°, V = 2262·9 Å^3, D_x = 1·791 (2) g cm^{-3}, μ = 27·64 cm^{-1}, R = 0·043 for 3950 reflections. At 183 (4) K, a = 9·766 (3), b = 14·850 (8), c = 16·806 (6) Å, β = 115·24 (3)°, V = 2204·6 Å^3, D_x = 1·838 (4) g cm^{-3}, μ = 28·37 cm^{-1}, R = 0·054 for 6128 reflections. The two crystallographically independent molecules (A and B) are similar and both have the expected geometry and dimensions. Each molecule is part of a chain of crystallographically equivalent molecules with short intermolecular N···I distances [3·243 (8) and 3·180 (8) Å at 297 K] and approximately linear C—N···I—C in each chain. There is disorder such that between 1 and 2% of the molecules appear to have I and CN interchanged; presumably any particular chain is ordered but 1 to 2% of the chains are in the opposite direction to the majority.

Introduction. As part of a study of intermolecular donor–acceptor interactions in crystals we have looked for examples of interactions between nitrile N atoms and I atoms in *p*-iodobenzonitrile (Schlemper & Britton, 1965), *o*-iodobenzonitrile (Lam & Britton, 1974) and 2,6-dibromo-4-iodobenzonitrile (Gleason & Britton, 1978). The expected interaction was found in the two compounds with I *para* to the CN but not in the *ortho* compound, where iodine–iodine and nitrile–nitrile interactions occurred. We report here the crystal structure of another member of this series. The structure has been determined at two temperatures, 297 and 183 K. This was carried out in response to a referee's comment on the disorder reported in the 297 K determination (see below).

Experimental. The compound was prepared as described by McNamara & Gleason (1976) and recrystallized from ethanol. Experimental data are given in Table 1. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Systematic extinctions ($0k0$, k odd; $h0l$, l odd) uniquely determined the space group. Data were collected using ω scans. Absorption corrections were made using *DIFABS* (Walker & Stuart, 1983). The unit cell was very similar to that of the analogous bromine compound (Kronebusch, Gleason & Britton, 1976*a*) and the positional parameters from that structure were successfully used to provide a trial structure. The structure was refined with full-matrix least-squares refinement on F's. All non-H atoms were given anisotropic thermal parameters; H atoms were included at idealized positions with isotropic B values 20% larger than the equivalent isotropic B value of the attached atom. Refinement of the initial data set (297 K) converged with R = 0·044, wR = 0·048 and S = 1·58; $w = 1/\sigma^2(F)$ was calculated from $\sigma^2(I) = \sigma^2(I)_c + (0{\cdot}04I)^2$, where $\sigma(I)_c$ is the standard deviation in I based solely on counting statistics. However, the C1—N1 and C2—C1 distances were abnormal [for example, the C1—N1 distances were 1·027 (8) and 1·074 (8) Å, respectively, shorter than usual and in poor agreement with each other]. The possibility of disorder was considered, and tested by including an I atom 2·10 Å from each C2 atom with fixed positional parameters and fixed isotropic B = 4·60 Å^2, the average of the equivalent isotropic B's of

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